Lecture 5

Thermal Oxidation of Silicon

Recap: Lecture 3 Wafer Clean and Wet Processing

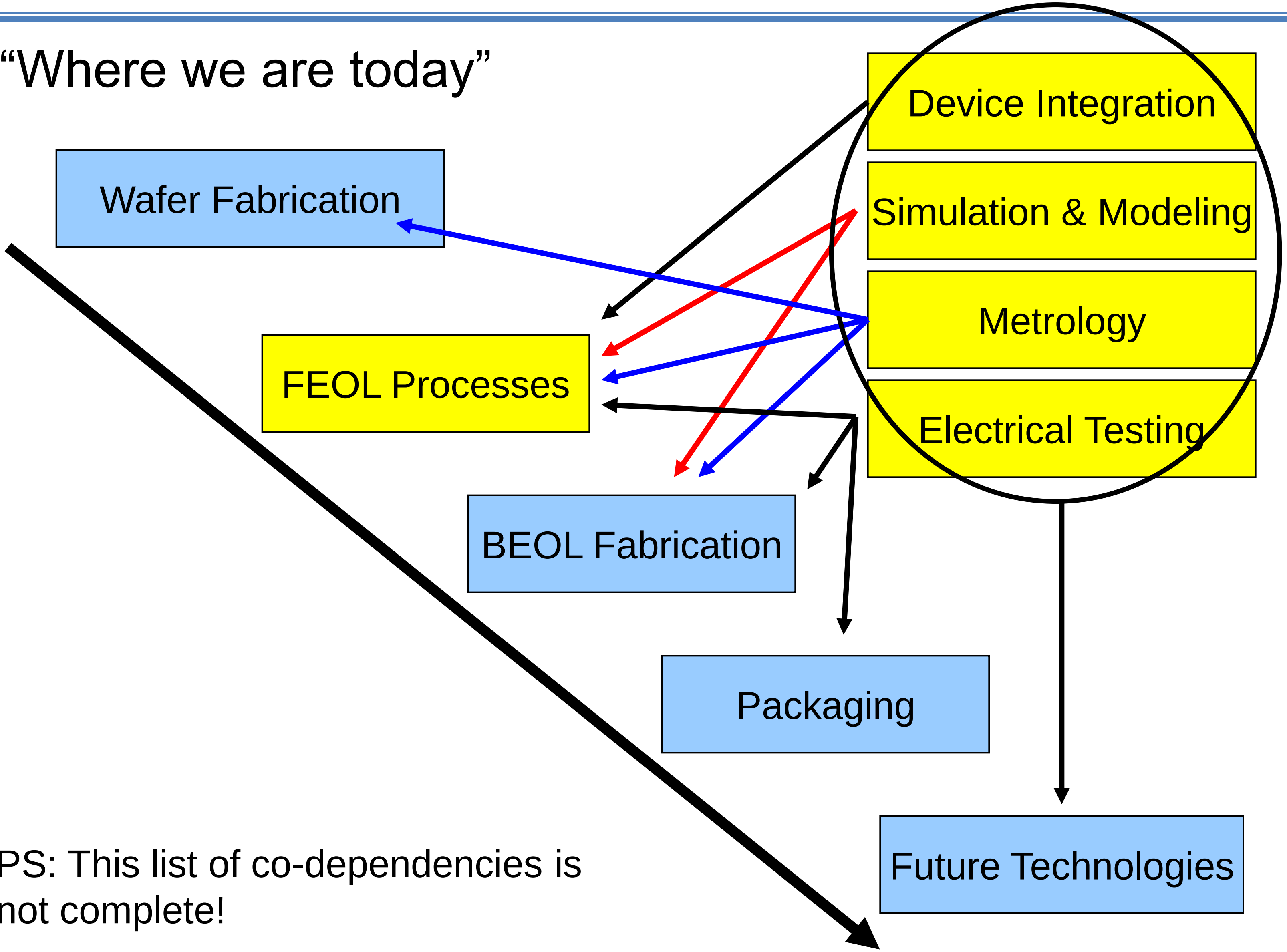
3 Level Approach

1. Clean room
2. Wafer cleaning
   - Contaminations: Particles, Organics, Metals, Native oxide
   - Cleaning Necessity:
     - Devices: Minority carrier lifetime↓, V_T changes, Ion↓ Ioff↑, Gate breakdown voltage ↓, Reliability ↓
     - Circuit: Yield↓, Electrical performance↓
3. Gettering (Lecture 2 & 3)

The bottom line is chip yield. “Bad” die manufactured alongside “good” die. Increasing yield leads to better profitability in manufacturing chips.

Lecture 5: Thermal Oxidation of Silicon

"Where we are today"



Wafer Fabrication

FEOL Processes

BEOL Fabrication

Packaging

Future Technologies

Device Integration

Simulation & Modeling

Metrology

Electrical Testing

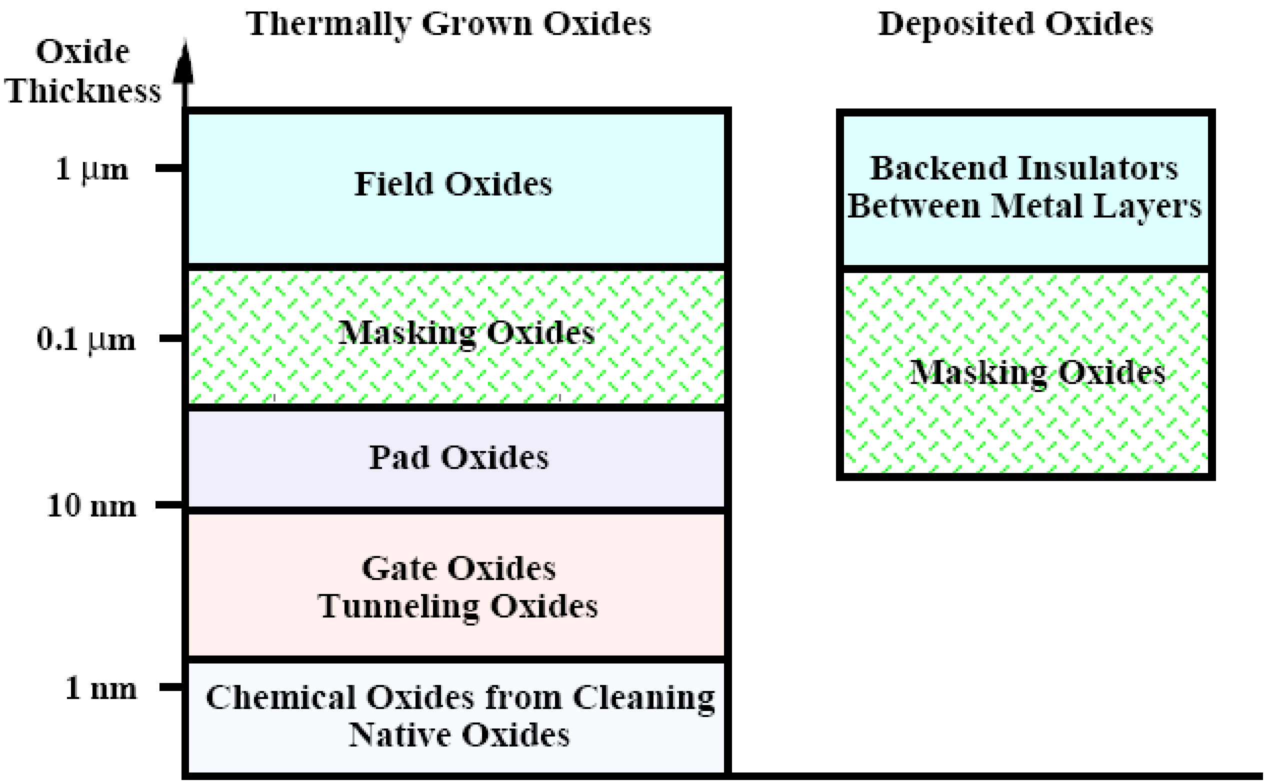
PS: This list of co-dependencies is not complete!

Thermal Oxidation of Silicon: Outline

- **Applications**
- **Properties and fabrication**
- **Linear parabolic model (Deal-Grove Model)**
- **Extensions of model**
- **Defects in SiO_2**
- **Characterization (recap from Lecture 4)**

Applications of Thermally Grown Oxides

Field oxide for isolation (e.g. LOCOS)
Pad, screen and masking oxides during implant, diffusion, etc.
Tunnelling oxides in EEPROM (flash memories)
Was used as gate oxide in MOS: until 45 nm CMOS
Was used for passive devices: capacitor dielectric in DRAMs



(Plummer Fig 6-1 p. 288)

Equivalent oxide thickness t_{ox}: Thickness of arbitrarily oxide re-calculated to corresponding SiO_2 thickness

Thermal Oxidation of Silicon: Outline

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- Linear parabolic model (Deal-Grove Model)
- Extensions of model
- Defects in SiO_2
- Characterization (recap from Lecture 4)

Basic Properties of SiO_2

- Usually thermally-grown SiO_2 is amorphous
- Melting point: 1700 °C
- Mass density: 2.27 g/cm^3
- Molecular density: 2.2×10^{22} $/cm^3$
- Refractive index n=1.46
- Dielectric constant $\varepsilon = 3.9$

High K
EOT

Basic Properties of SiO_2

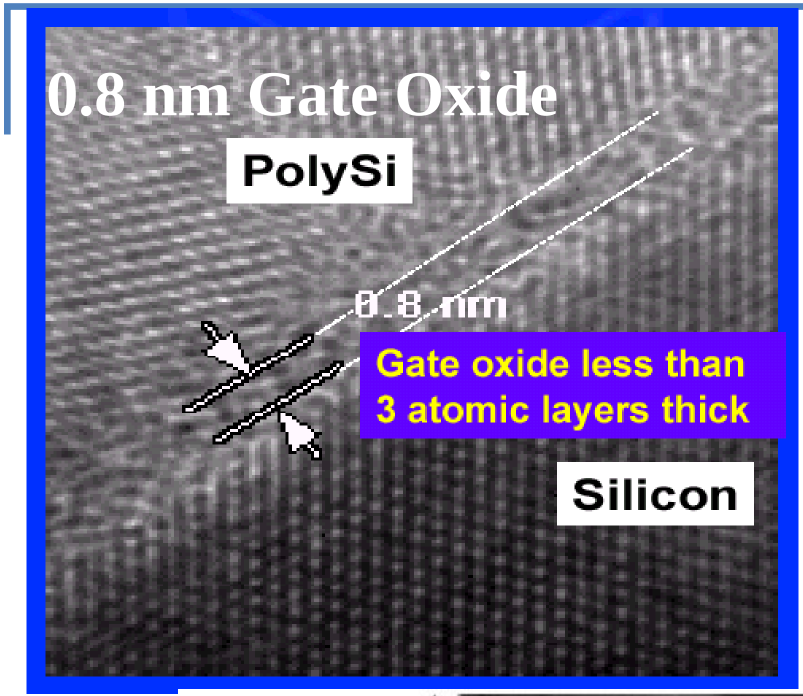
- **Easily selectively etched**

- **Mask for most common impurities (B, P, As, Sb) (Low diffusivity for all dopants of Si)**
- **Excellent Insulator ($\rho > 10^{16}$ Ωcm, E_g>9 eV)**

- **High breakdown field (> 10^7 V/cm)**

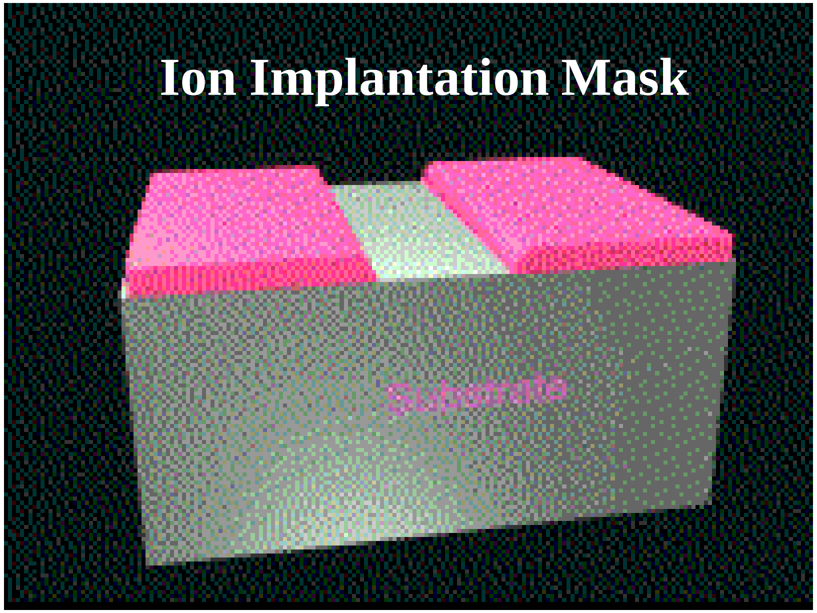
- **Stable bulk electric properties (> 900°C, > 10^{-9} Torr)**

- **Stable and reproducible interface with Si**



0.8 nm Gate Oxide

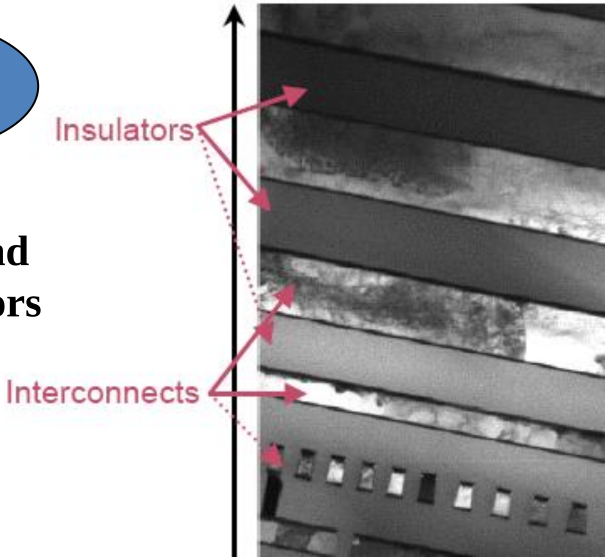
Gate oxide less than 3 atomic layers thick



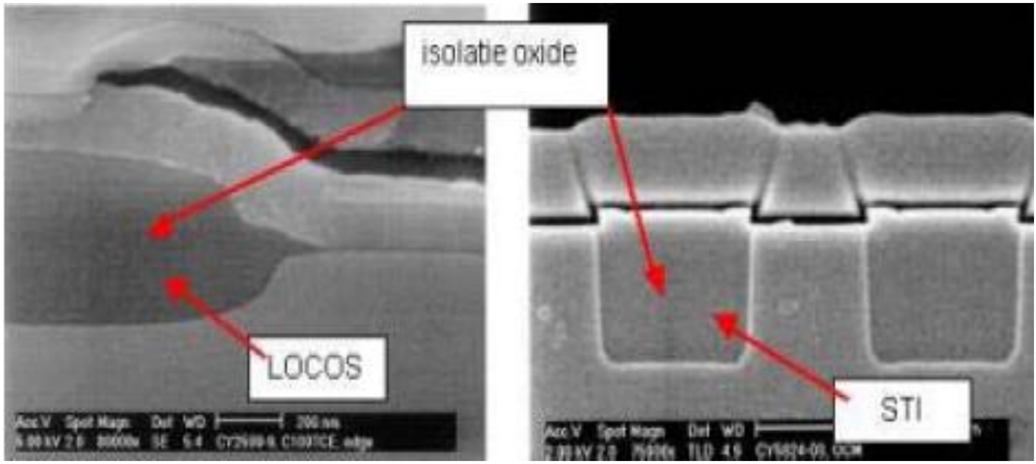
Ion Implantation Mask

Low k

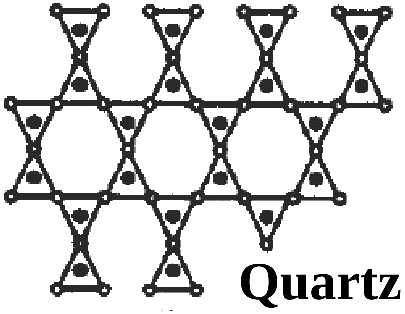
Back-end Insulators



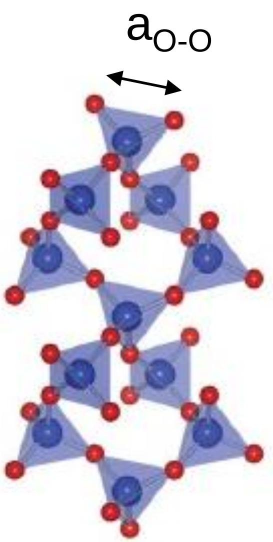
Isolation



SiO_2 Structure



Quartz

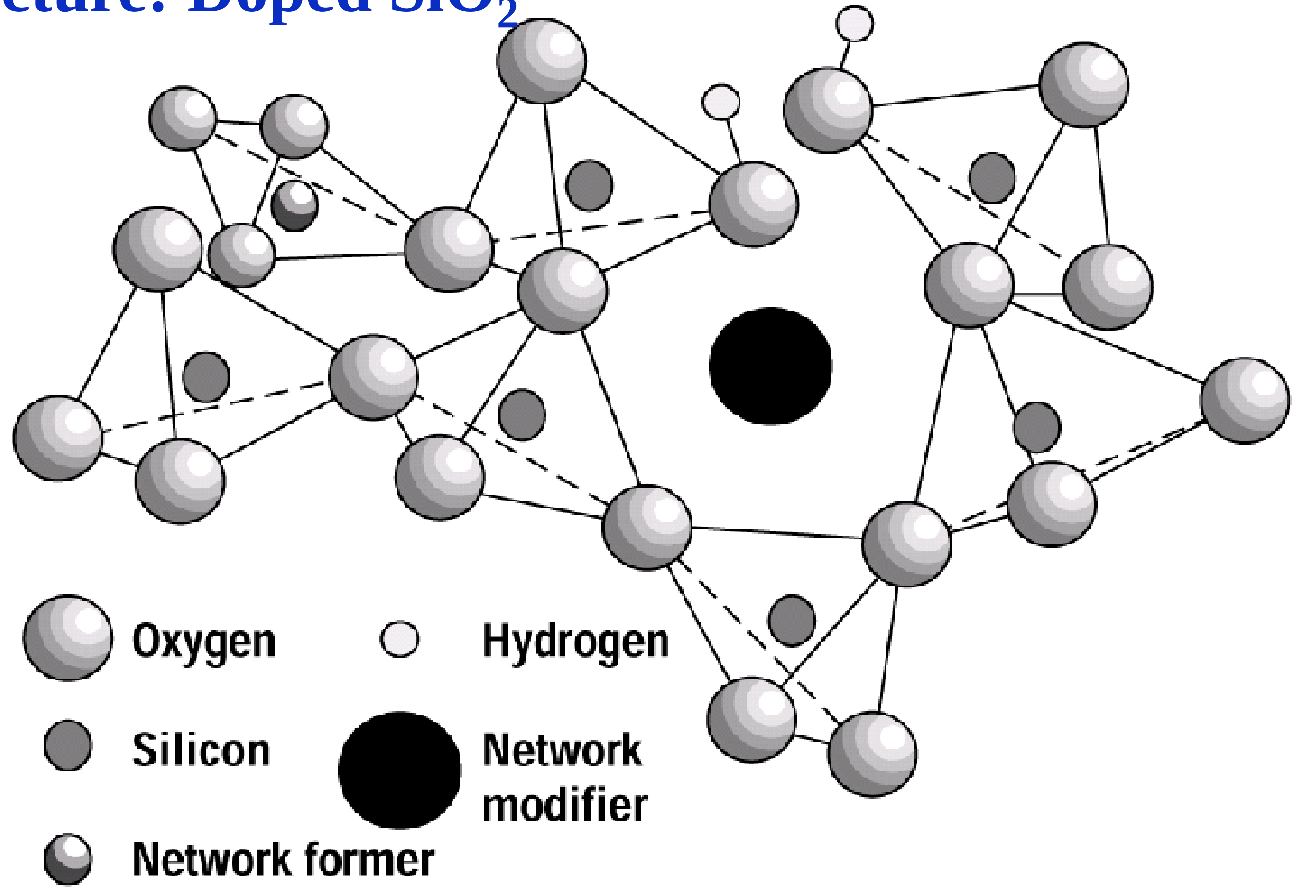


α-SiO_2

- Classification
  - Crystalline: Quartz, etc.
  - Amorphous (α-SiO_2)

- Made up of Si—O tetrahedron
  - Silicon atom lies in the tetrahedral center and oxygen atoms at the four vertices
  - Tetrahedrons are connected by Si-O-Si
  - Oxygen atoms connecting two silicon atoms are called bridging oxygen or oxygen bridge
  - $a_{Si\text{-}O} = 0.162$ nm
  - $a_{O\text{-}O} = 0.262$ nm

SiO_2 Structure: Doped SiO_2



- Network former leads to e.g. borosilicate glass, lead glass
- Network modifier converts bridging oxygen atoms into non-bridging oxygen atoms

Overall Oxidation Reaction

- **Dry Oxidation**

$$Si(s) + O_2(g) \rightarrow SiO_2(s)$$

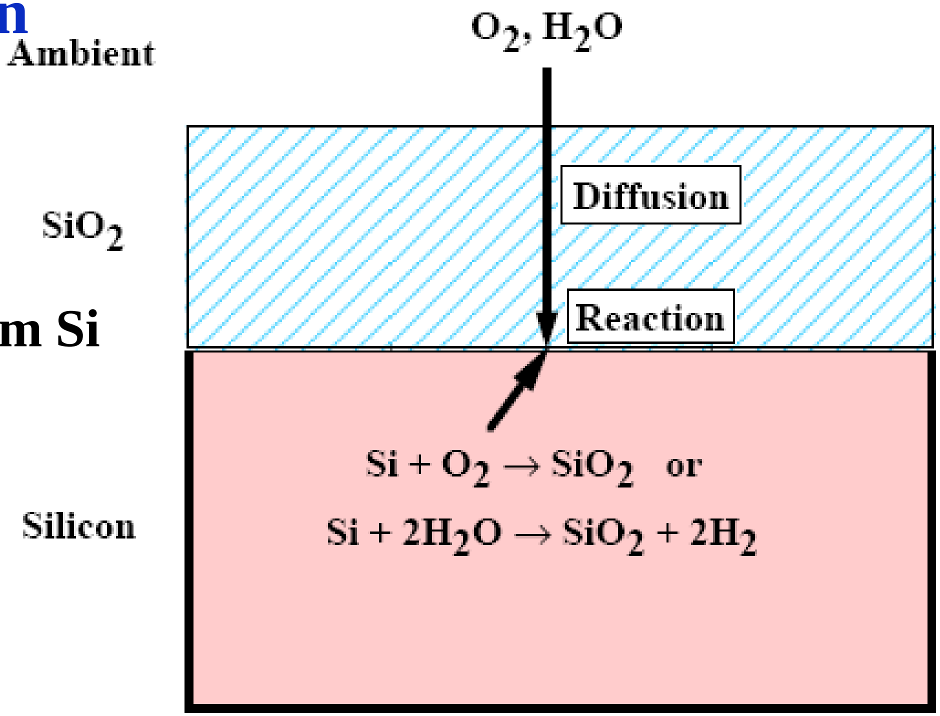
- **Wet/Steam Oxidation**

$$Si(s) + 2H_2O(g) \rightarrow SiO_2(s) + 2H_2(g)$$

✓ **Both reactions happen at 700 ~1200 ºC**

✓ **Steam Oxidation is about 10 times faster than Dry Oxidation**

Oxidation: Volume Expansion

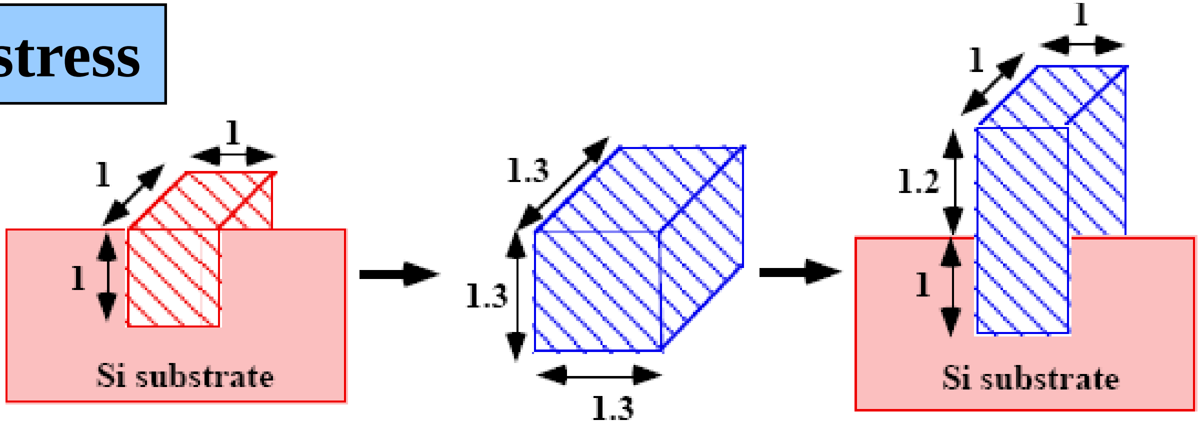


Oxide growth consumes Si

1-mm-thick SiO_2 consumes 0.45 mm Si

Volume Expansion (~ 2.2 times)

SiO_2 suffers from stress

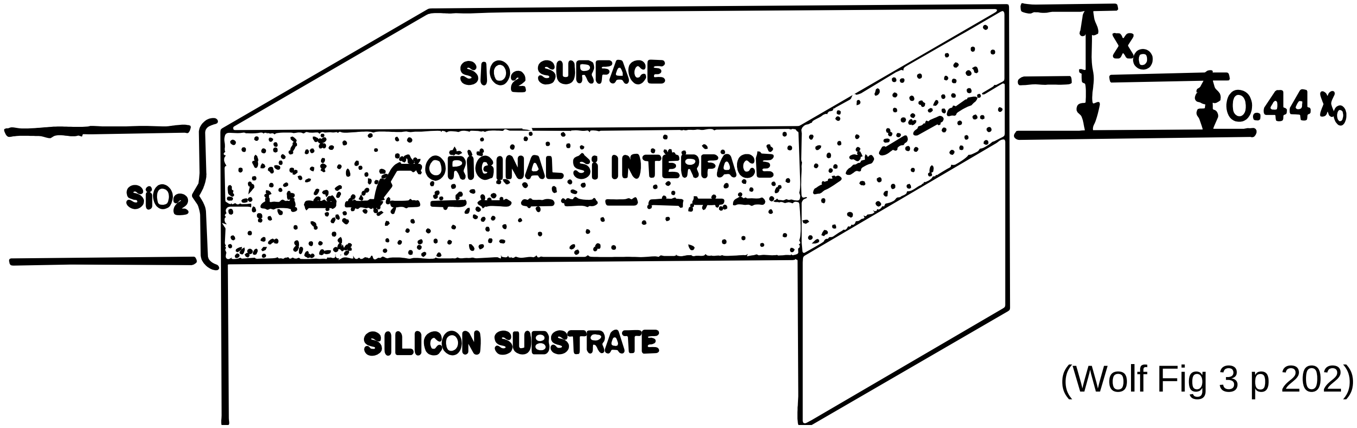


Oxidation: Basic reactions

Dry oxidation: $Si(s) + O_2(g) \rightarrow SiO_2(s)$

Wet oxidation: $Si(s) + 2H_2O \rightarrow SiO_2(s) + 2H_2(g)$

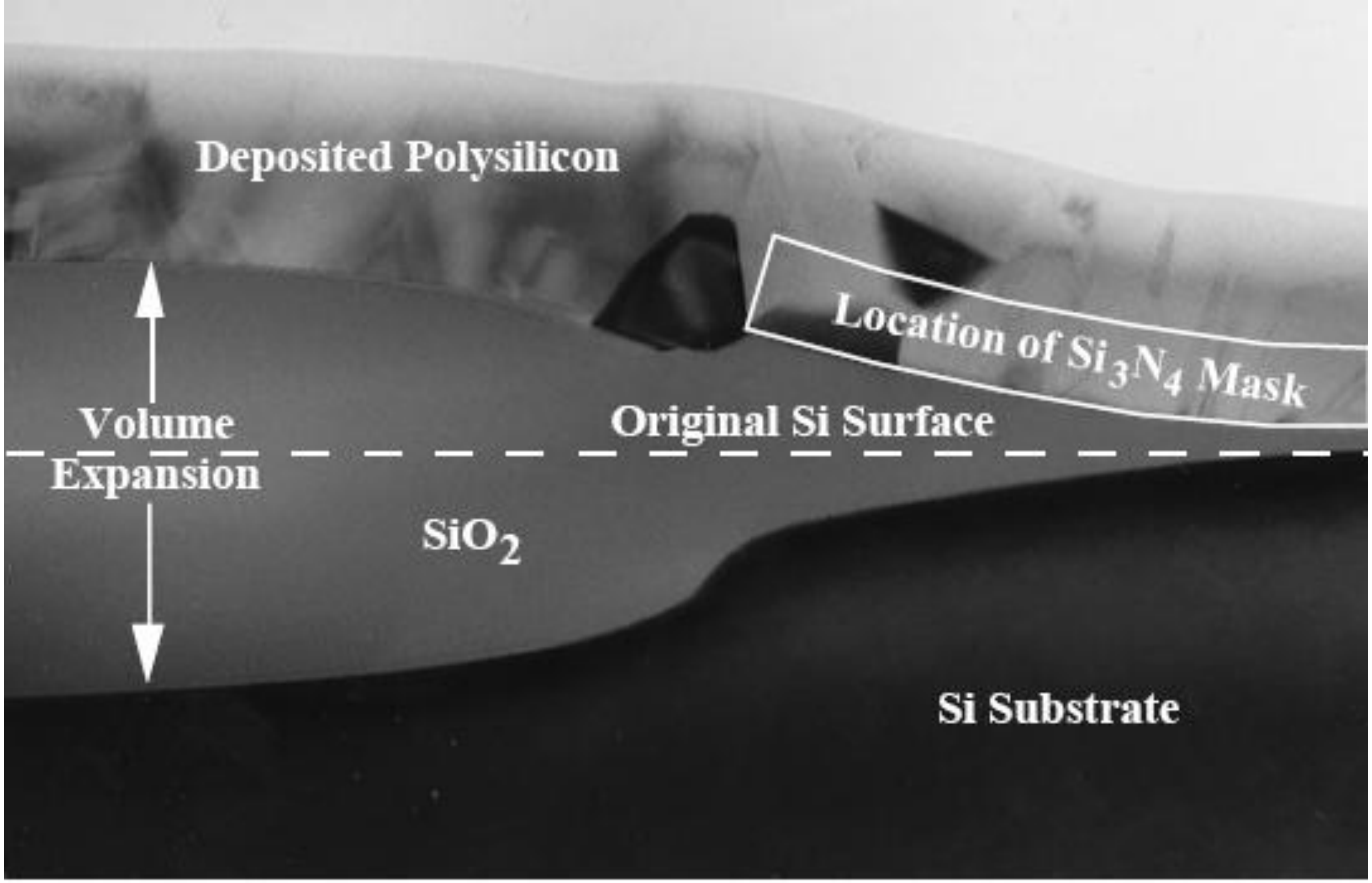
Oxidation by inward diffusion of oxidant through the growing oxide to the interface



(Wolf Fig 3 p 202)

Very good adhesion to Si leads to volume expansion upwards
→ *compressive stress* in SiO_2

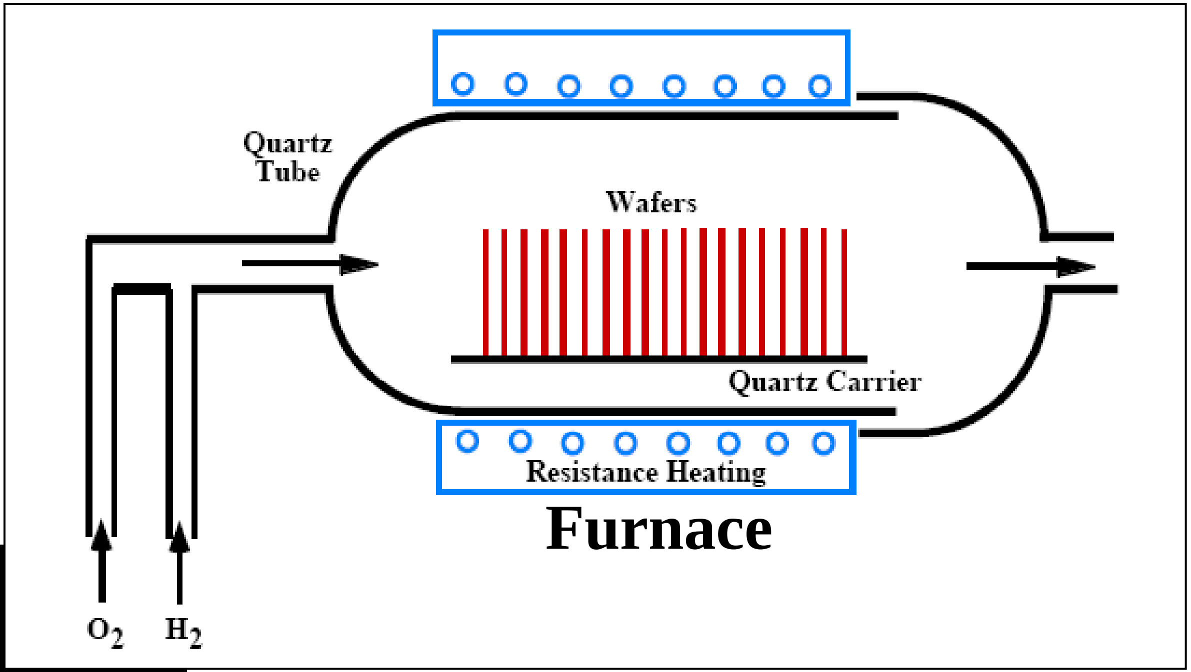
Oxidation: Example LOCOS

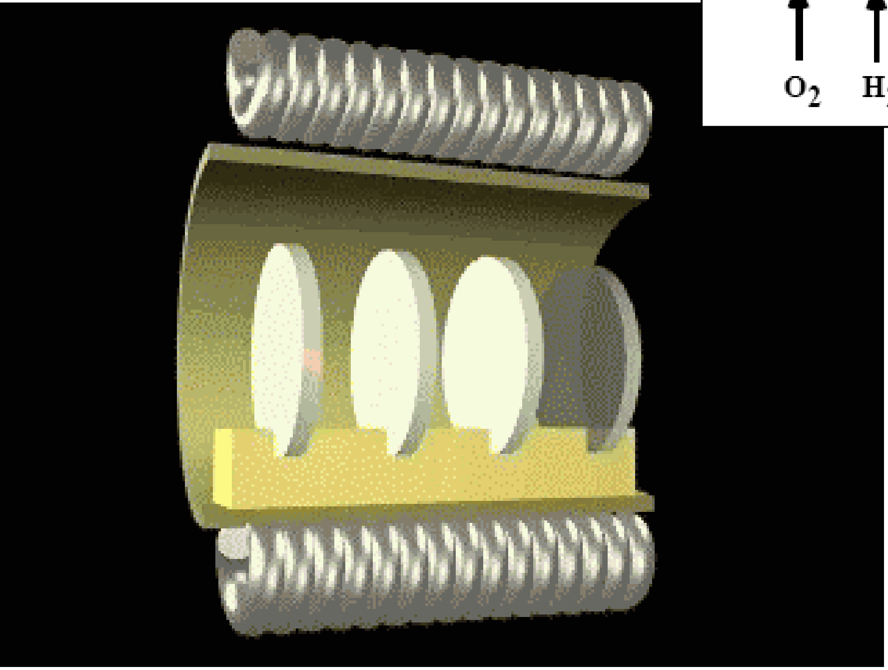


(Photo courtesy of J. Bravman.)

In LOCOS, SiO_2 volume is 2.2 times larger than that of oxidized Si

Oxidation Methods





- Thermal Oxidation
- Chlorine Doping Oxidation
- H_2-O_2 Reaction Oxidation
- High-Pressure Oxidation

Oxidation Equipment

Different types of furnace oxidation

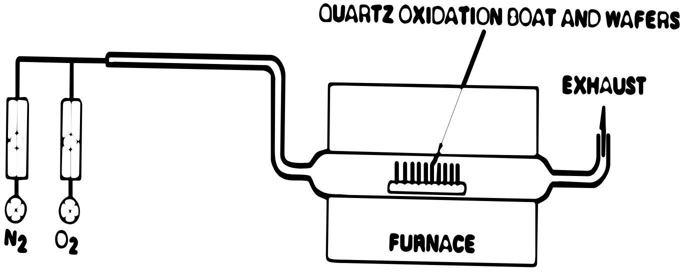
Here: Furnace oxidation using dry (O_2) or wet (H_2O) ambient

Typically 800- 1200°C at atmospheric pressure (1 atm)

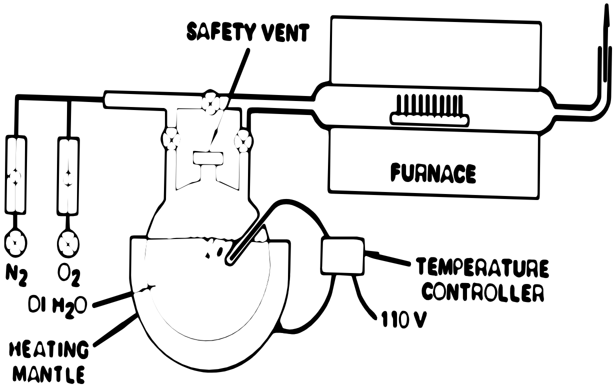
Chlorine may be added by

- HCl
- TCE
- TCA or trans-LC

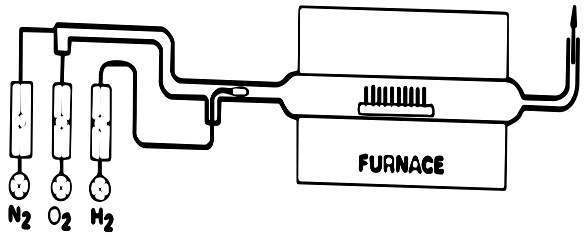
→ gettering of impurities



A. DRY O_2 OXIDATION



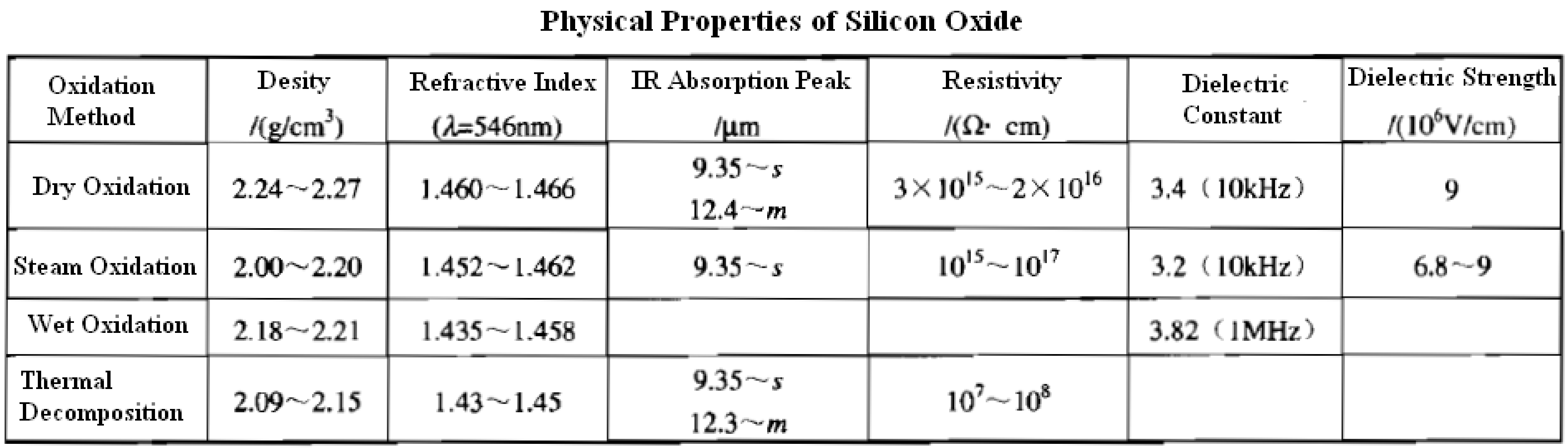
B WET OXYGEN OXIDATION



C. PYROGENIC STEAM OXIDATION

1142A

Properties of SiO_2 from different fabrication methods



Physical Properties of Silicon Oxide

Oxidation Method	Desity /(g/cm^3)	Refractive Index (λ=546nm)	IR Absorption Peak /µm	Resistivity /(Ω· cm)	Dielectric Constant	Dielectric Strength /(10^6V/cm)
Dry Oxidation	2.24~2.27	1.460~1.466	9.35~*s* 12.4~*m*	3×10^{15}~2×10^{16}	3.4（10kHz）	9
Steam Oxidation	2.00~2.20	1.452~1.462	9.35~*s*	10^{15}~10^{17}	3.2（10kHz）	6.8~9
Wet Oxidation	2.18~2.21	1.435~1.458			3.82（1MHz）	
Thermal Decomposition	2.09~2.15	1.43~1.45	9.35~*s* 12.3~*m*	10^7~10^8		

Thermal Oxidation of Silicon: Outline

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- **Linear parabolic model (Deal-Grove Model)**
- Extensions of model
- Defects in SiO_2
- Characterization (recap from Lecture 4)

Deal－Grove Model: Silicon Thermal Oxidation Model

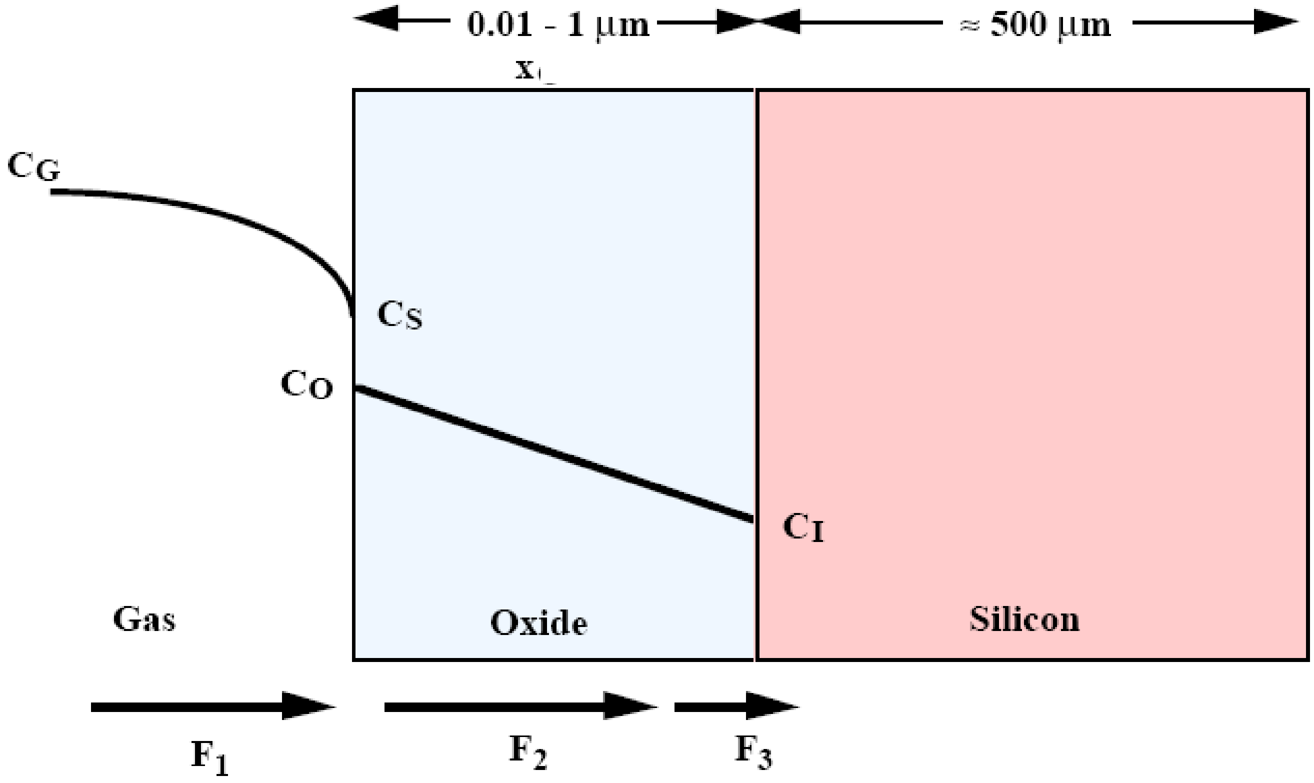
Deal－Grove Model (linear-parabolic model)

- B.E. Deal and A.S. Grove, "General Relationship for the Thermal Oxidation of Silicon“, Journal of Applied Physics 36 (12): 3770–3778, 1965
- Use solid state theory to explain 1D planar growth of SiO2

Apply to:

- Oxidation temperature range: 700~1200 ^{o}C
- Local pressure 0.1~25 atm.
- Wet and Dry Oxidation with oxide thickness within 20~2000 nm

Deal－Grove Model: Silicon Thermal Oxidation Model



Oxidant Concentration

C_G: in gas flow

C_S: outside oxide surface

C_O: inside oxide surface

C_I: at the interface

F_1: Flux of gas transport

F_2: Diffusion Flux through SiO_2

F_3: Reaction Flux at the Si/SiO_2 interface

F: number/(cm^2-s)

C : number/cm^3

Deal－Grove Model: Silicon Thermal Oxidation Model

F_1: Flux of oxidant diffusing from gas phase region to oxide surface

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

h_g: Mass transfer coefficient, cm/s

C: Gas concentration, molecules/cm^3

F : Flux, molecules/(cm^2-s)

1. **Ideal Gas Law:** $P_S V = NkT$, so $C_S = N/V = P_S/kT$

   P_s: *Surface gas pressure*

   V: *Volume*

   N: *Number of molecules*

   k: *Boltzmann constant*

   T: *Temperature*

Deal－Grove Model: Silicon Thermal Oxidation Model

F_1: Flux of oxidant diffusing from gas phase region to oxide surface

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

h_g: Mass transfer coefficient, cm/s
C: Gas concentration, molecules/cm^3
F : Flux, molecules/(cm^2-s)

$$C_S = N/V = P_S/kT$$

2. **Henry's Law:** **The equilibrium concentration of a gas species dissolved in a solid is proportional to the partial pressure of that species at the solid surface (H = const.).**

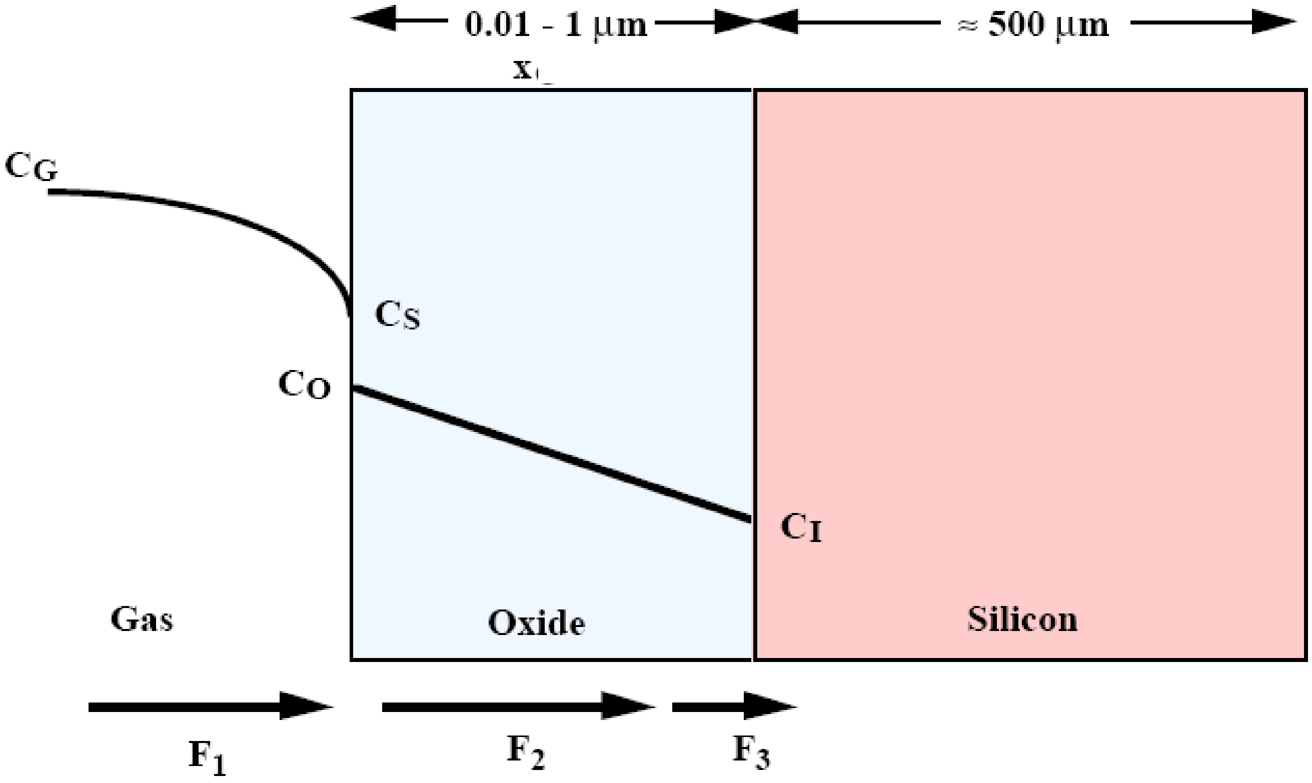
$$C_O = HP_S$$

$$F_1 = h_g(C_G - \frac{P_S}{kT}) = h_g(C_G - \frac{C_O}{HkT})$$

Setting $h = h_g/HkT$, $C_G = C^*/HkT$

$$F_1 = h(C^* - C_O)$$

Deal－Grove Model: Silicon Thermal Oxidation Model



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Deal－Grove Model: Silicon Thermal Oxidation Model

F_2: Flux of oxidant diffusing through oxide to the Si/SiO2 interface

Fick's 1st Law of Diffusion

$$F_2 = D\frac{\delta C}{\delta x} = D\frac{C_O - C_I}{x}$$

Assumption:
Steady state
No oxidant loss

Derivative becomes gradient

***D*: Oxidant diffusivity in the oxide, cm²/s**

F_3: Flux of oxidant reacting at the Si/SiO$_2$ interface

$$F_3 = k_s C_I$$

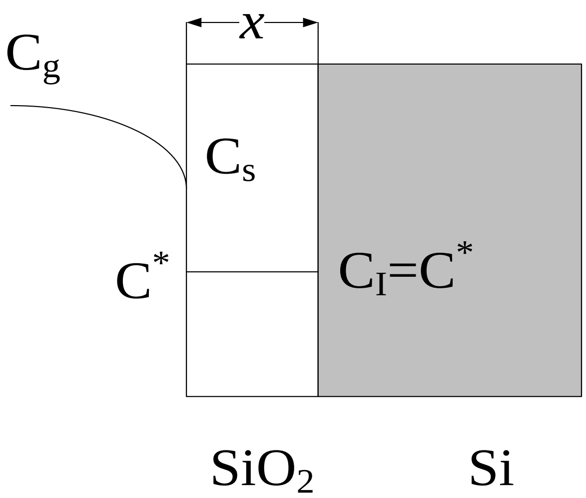
k_s: Interface reaction rate constant, cm/s

Deal－Grove Model: Silicon Thermal Oxidation Model

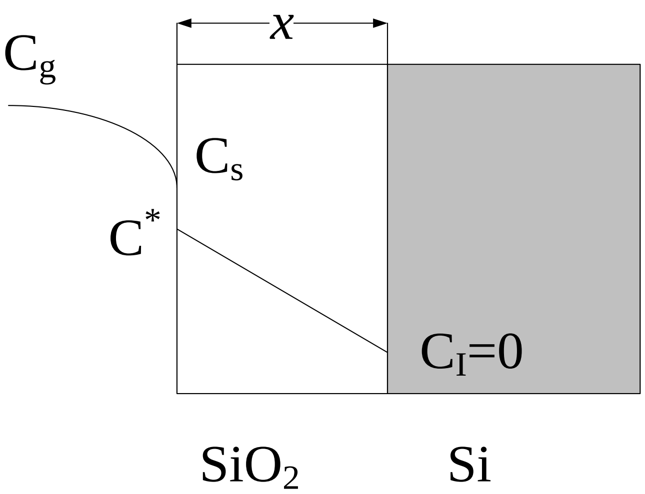
Under Steady-state conditions, $F_1 = F_2 = F_3$

$$C_I = \frac{C^*}{1 + \frac{k_s}{h} + \frac{k_s x}{D}}$$

- **At $k_s x/D \cong 1$, oxidation transits from reaction limited to diffusion limited**
- **Transition at oxide thickness from 50-200 nm**
- **k_s and D change with temperature**



$k_s x/D$<<1, Reaction rate controlled



$k_s x/D$>>1, Diffusion controlled

Deal－Grove Model: Silicon Thermal Oxidation Model

Combining formula for F_3 and C_I, we define

Growth Rate

$$R = \frac{F}{N_1} = \frac{dx}{dt} = \frac{k_S C^*}{N_1\left[1 + \frac{k_S}{h} + \frac{k_S x}{D}\right]}$$

N_1 is the number of oxidant in 1 cm^3 SiO_2
For O_2 oxidation, $N_1 = 2.2\times10^{22}$ cm^{-3}
For H_2O oxidation, $N_1 = 4.4\times10^{22}$ cm^{-3}

Integrate to describe growth kinetics:

$$N_1 \int_{x_i}^{x_0} \left[1 + \frac{k_S}{h} + \frac{k_S x}{D}\right] dx = \int_0^t k_S C^* dt$$

X_i: initial oxide thickness
X_0: final oxide thickness

Deal－Grove Model: Silicon Thermal Oxidation Model

$$N_1 \int_{x_i}^{x_0} \left[1 + \frac{k_S}{h} + \frac{k_S x}{D} \right] dx = \int_0^t k_S C^* dt$$

X_i: initial oxide thickness
X_0: final oxide thickness

1/*h* is ignored since *h* is very large (mass transport to oxygen surface not limiting factor)

Setting:

$B = 2DC^*/N_1$

$A = 2D(1/k_s + 1/h)$

and hence

$B/A \cong C^* k_s / N_1$**, leads to**

$$\boxed{\frac{x_0^2 - x_i^2}{B} + \frac{x_0 - x_i}{B/A} = t}$$

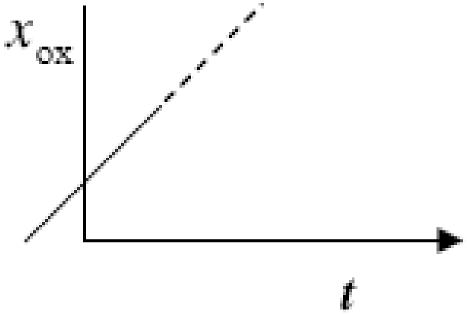
Deal－Grove Model: Silicon Thermal Oxidation Model

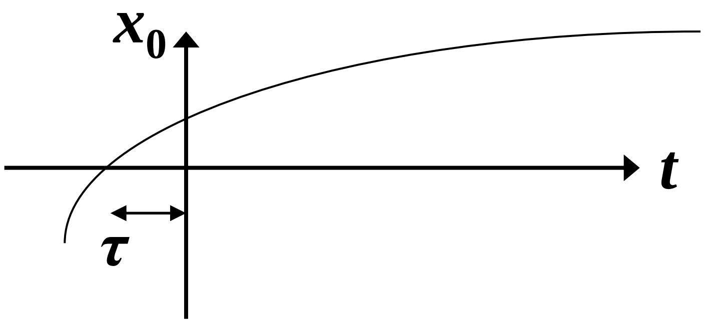
For convenience,

$$\boxed{\frac{x_0^2}{B}+\frac{x_0}{B/A}=t+\tau}$$ **where**

$B = 2DC^*/N_1$—parabolic rate constant, contribution from F_2 (Oxidant diffusion)
$B/A \cong C^*k_s/N_1$—linear rate constant, contribution from F_3 (Interface reaction)

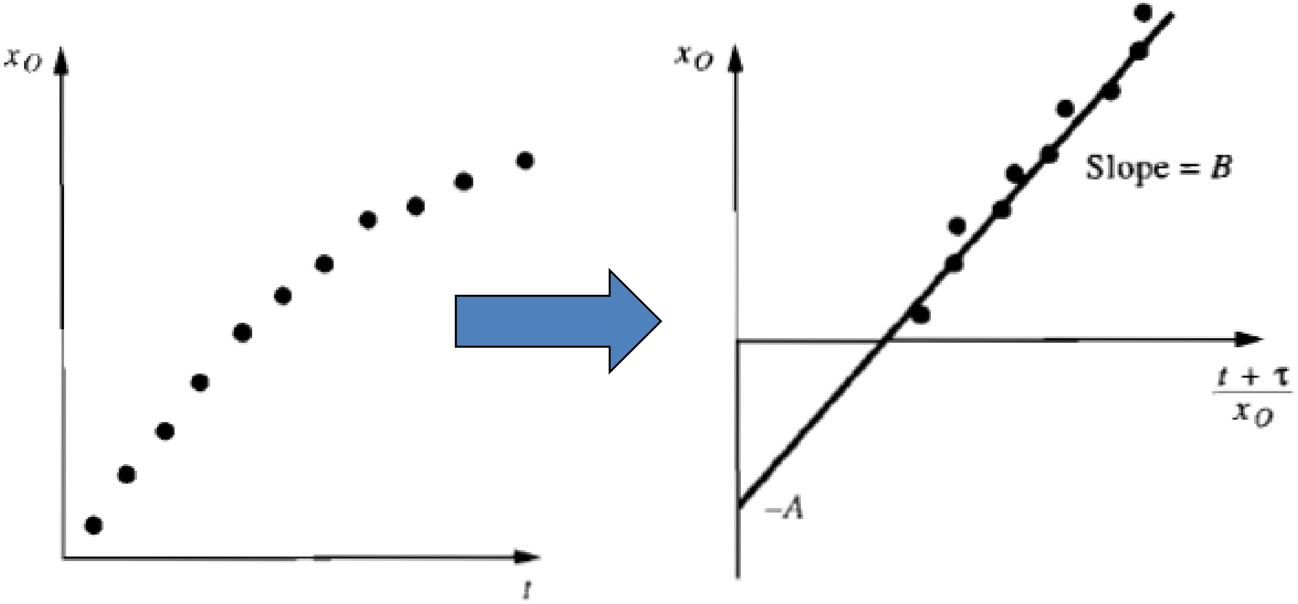
Two limits: **Thin oxide** **Thick oxide**





Deal－Grove Model: Silicon Thermal Oxidation Model

Extraction of B and B/A from experimental data



$$\frac{x_0^2}{B} + \frac{x_0}{B/A} = t + \tau \Rightarrow x_0 = B\frac{t+\tau}{x_0} - A$$

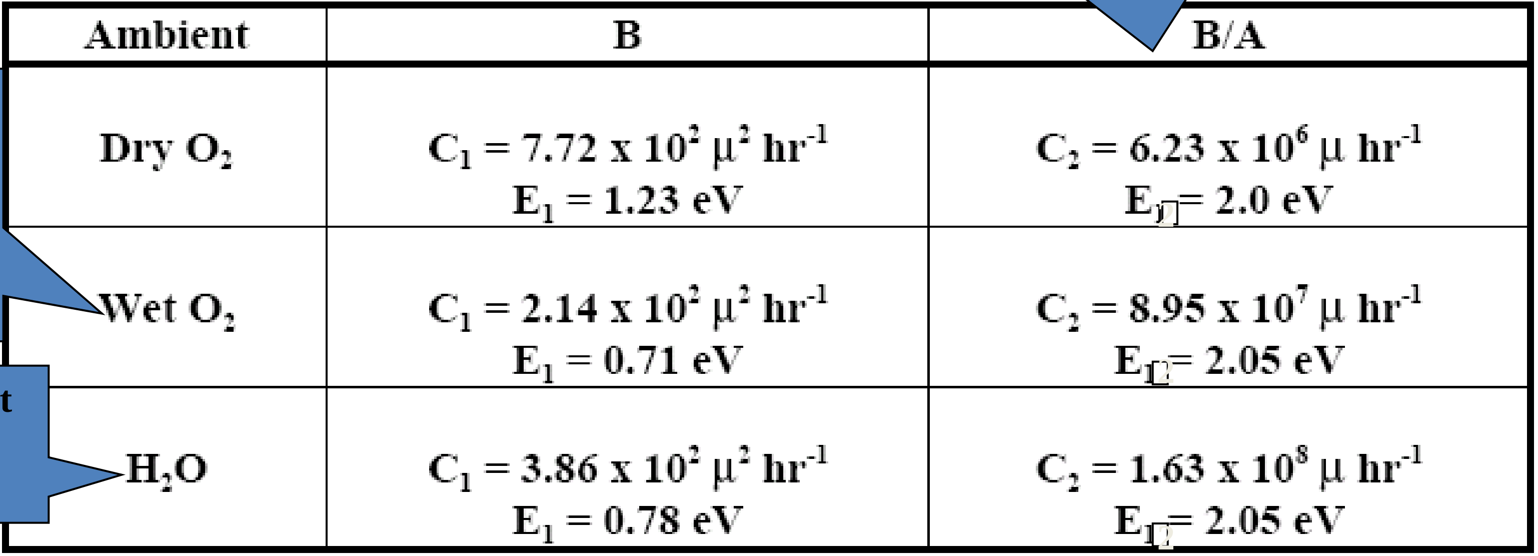
τ is provided by experiments

When oxidations are performed on flat unpatterned surfaces, on lightly doped substrates, in simple O_2 or H_2O ambients and when the oxide is thicker than about 20 nm, the growth kinetics are usually well described by the linear parabolic model. *B* and *B*/*A* are well described by Arrhenius expressions:

Oxidant diffusion: $$B = C_1 \exp(-E_1/kT)$$

Interface reaction: $$\frac{B}{A} = C_2 \exp(-E_2/kT)$$

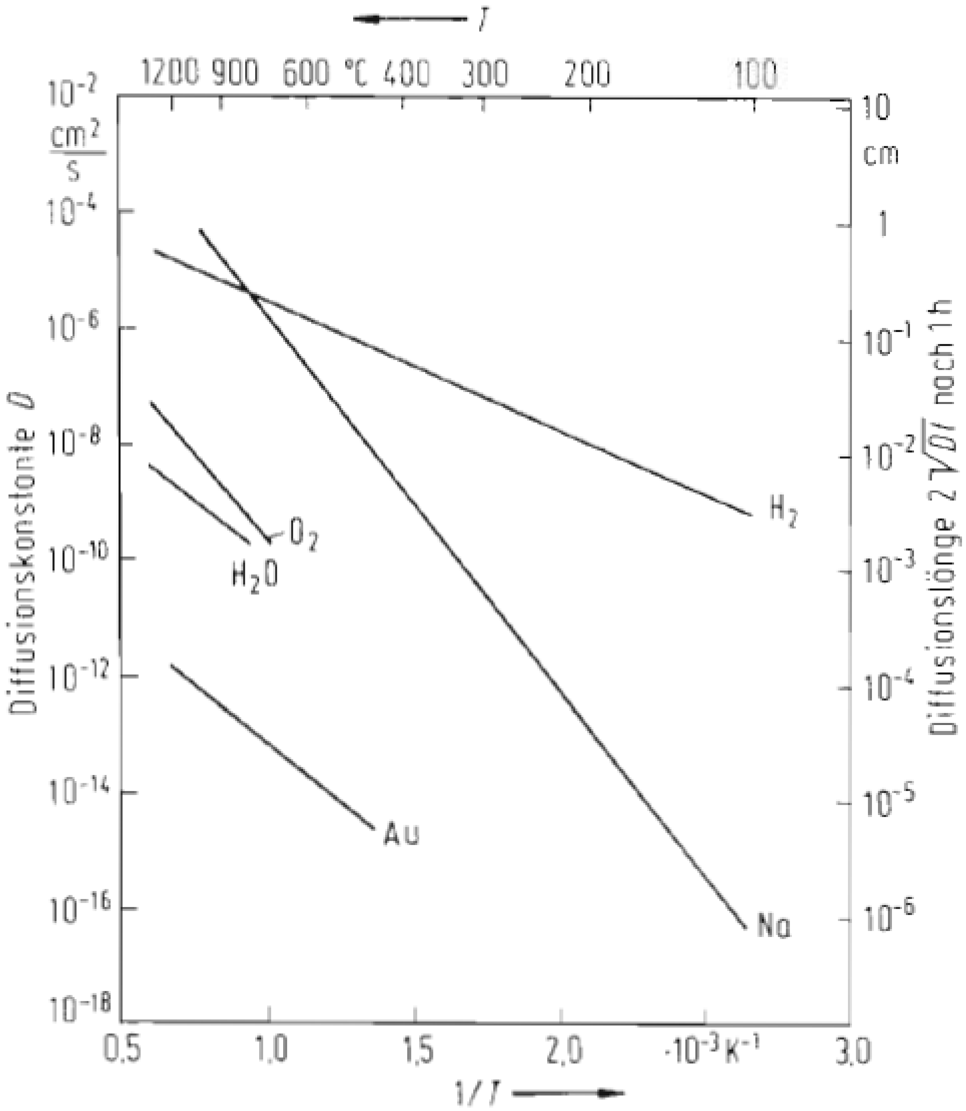
Rate constants describing (111) silicon oxidation kinetics at 1 atm. total pressure. For corresponding values for (100) silicon, all C_2 values should be divided by 1.68.



Ambient	B	B/A
Dry O_2	$C_1 = 7.72 \times 10^2\ \mu^2\ hr^{-1}$ $E_1 = 1.23$ eV	$C_2 = 6.23 \times 10^6\ \mu\ hr^{-1}$ $E_2 = 2.0$ eV
Wet O_2	$C_1 = 2.14 \times 10^2\ \mu^2\ hr^{-1}$ $E_1 = 0.71$ eV	$C_2 = 8.95 \times 10^7\ \mu\ hr^{-1}$ $E_2 = 2.05$ eV
H_2O	$C_1 = 3.86 \times 10^2\ \mu^2\ hr^{-1}$ $E_1 = 0.78$ eV	$C_2 = 1.63 \times 10^8\ \mu\ hr^{-1}$ $E_2 = 2.05$ eV

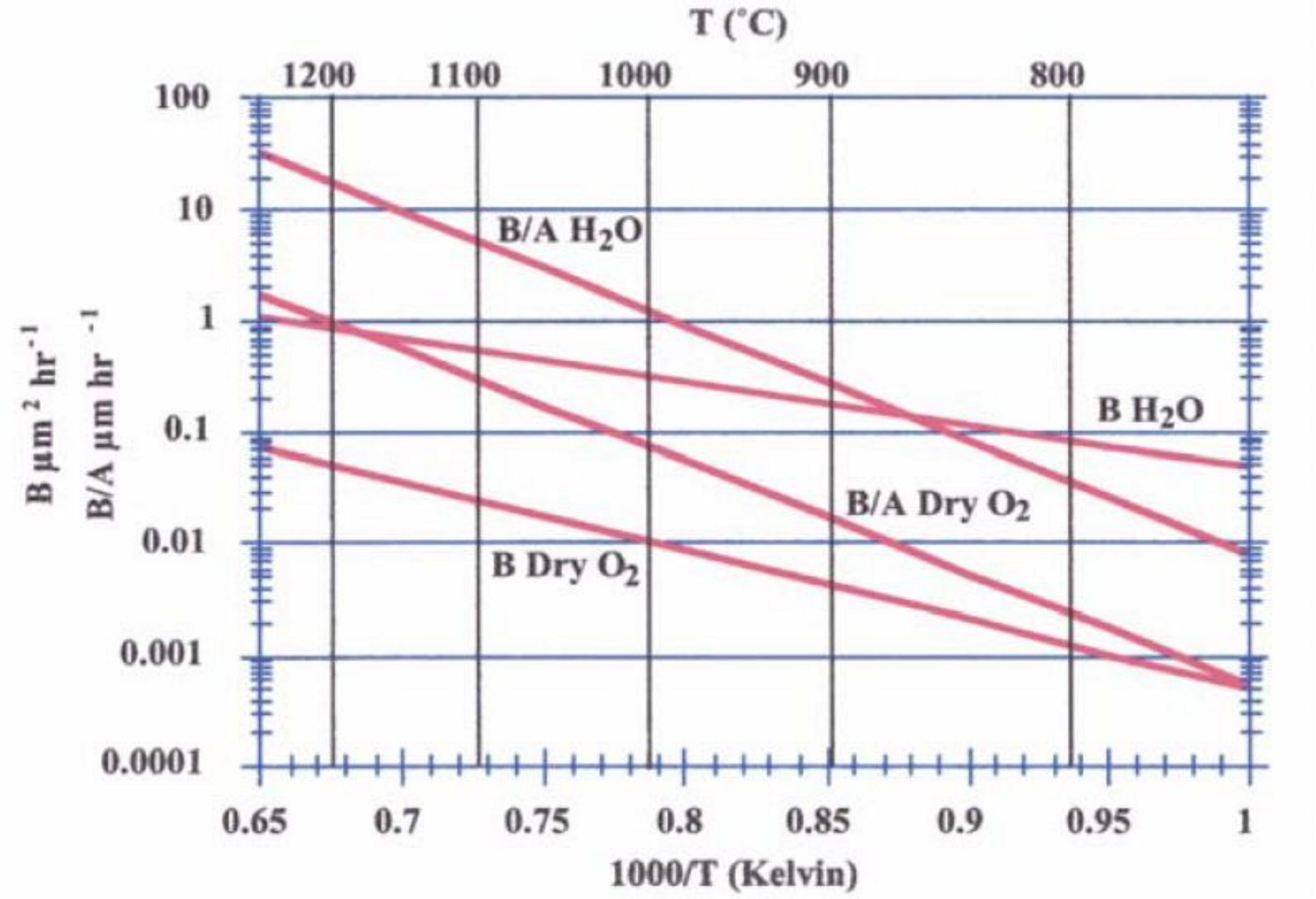
O_2 is bubbled through H_2O at 95 °C

H_2+O_2 react to produce H_2O



Diffusion constant of non doping elements in SiO_2

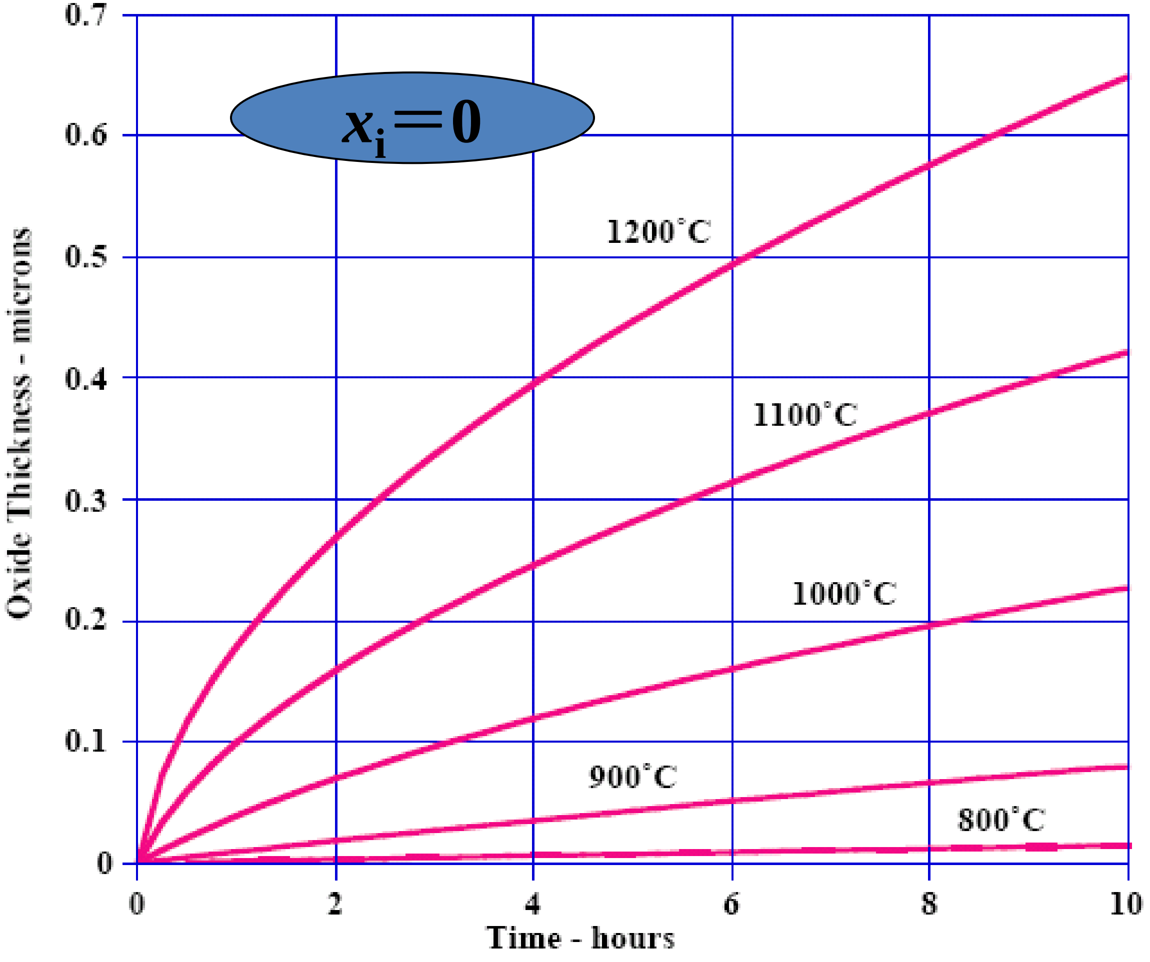
Deal－Grove Model: Temperature Dependence of B and B/A



B and B/A for O_2 and H_2O oxidation of (111) Si. Values taken from above table.

Deal－Grove Model: Example Dry O_2

Calculation based on D-G model:
Dry O_2 Oxidation

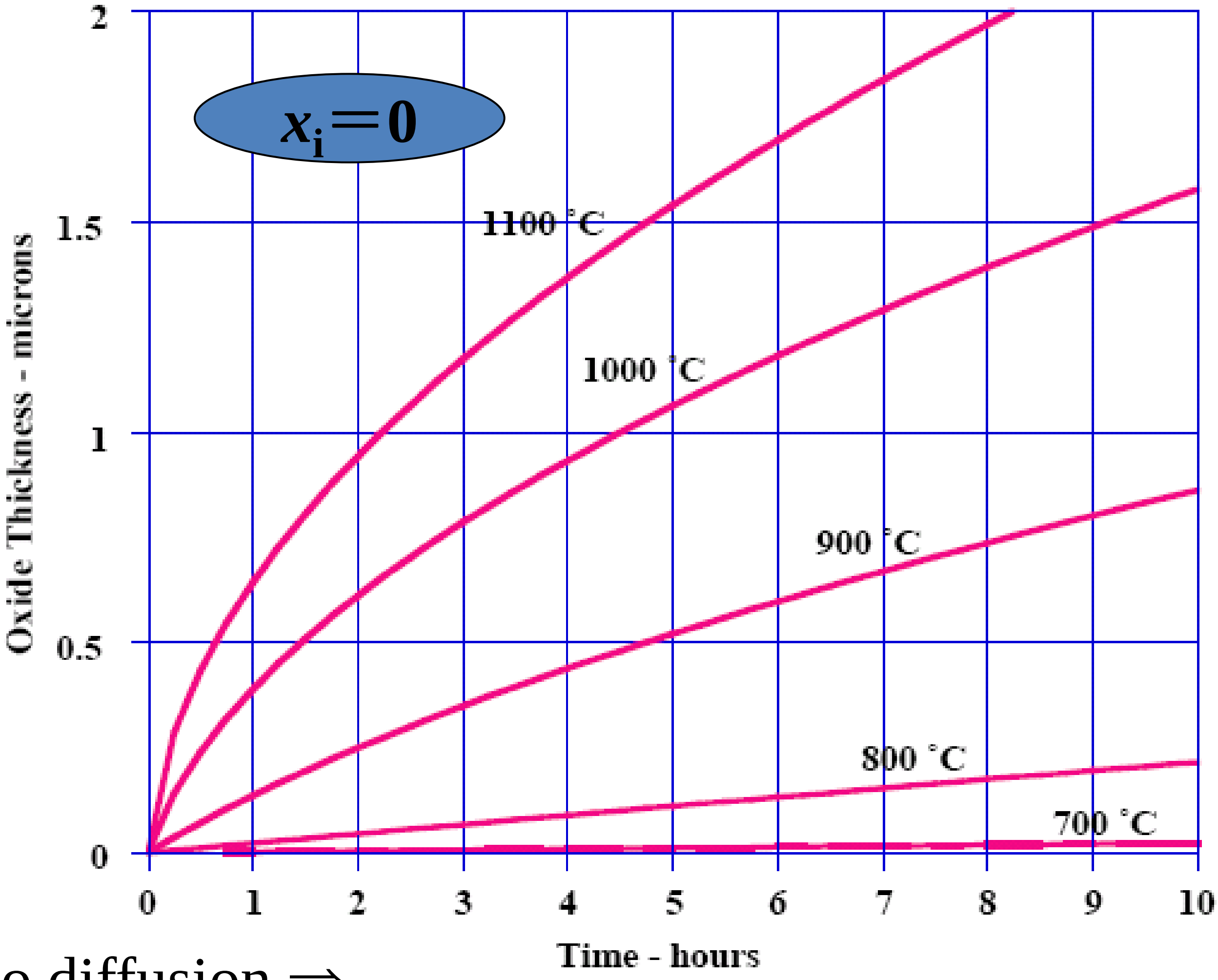


Applicable for ～100－200 nm

800-1200 °C,
1 atm, 0.1 µm/hr
High density ⇒ Gate oxidation, etc.

Deal－Grove Model: Example H_2O

Calculation based on D-G model:
H_2O Oxidation



Applicable for >100~200 nm

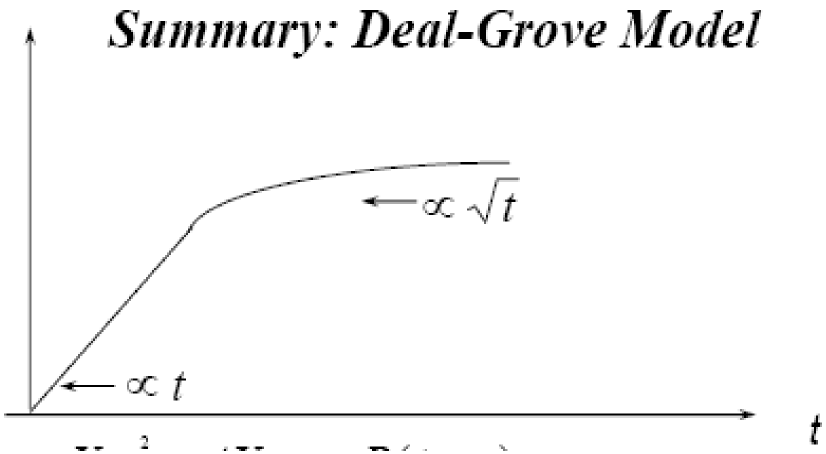
700-1100 ºC,
25 atm , 1 μm / hr

Loose, weak barriers to diffusion ⇒
Etching mask and Field oxidation

Summary: Deal – Grove Model

$$\left.\begin{aligned} &\frac{x_0^2}{B} + \frac{x_0}{B/A} = t + \tau \\ &\tau = \frac{x_i^2 + Ax_i}{B} \end{aligned}\right\}$$

Oxidation rate $$\frac{dx_0}{dt} = B/(2x_0 + A)$$



This equation describes well the growth kinetics under specific conditions:

- **✓Flat unpatterned surfaces**
- **✓Lightly doped substrates**
- **✓Simple O_2 or H_2O ambients**
- **✓Final oxide thickness > 20 nm**

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- Applications
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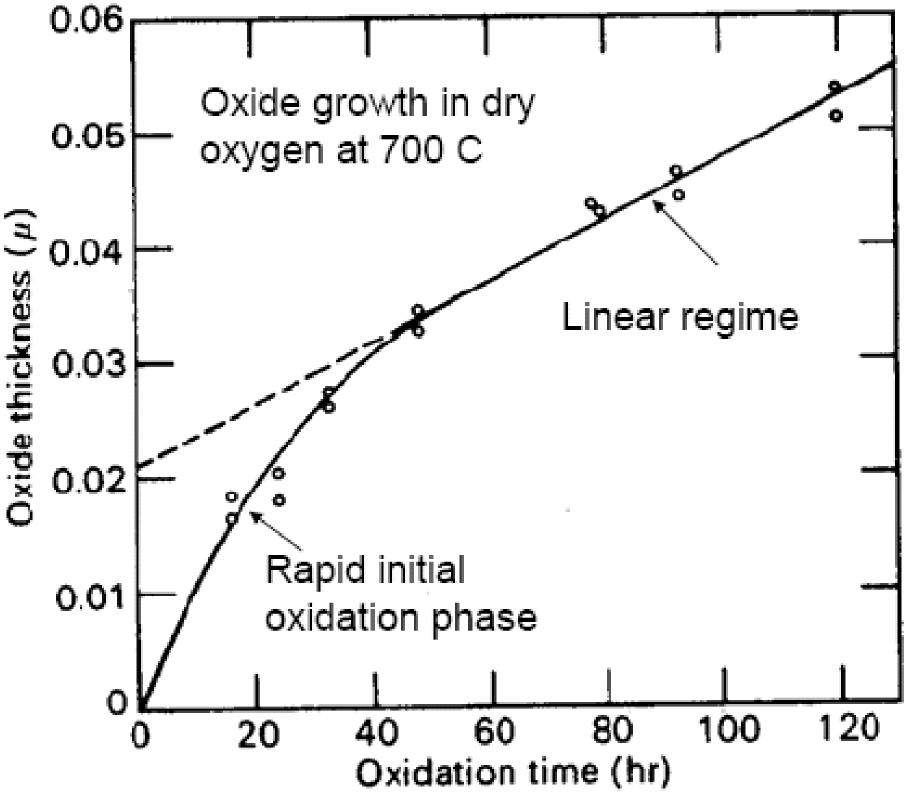
- Linear parabolic model (Deal-Grove Model)
- **Extensions of model**
- Defects in SiO_2
- Characterization (recap from Lecture 4)

Limitations of D-G Model: Thin Oxidation

- **D-G model cannot accurately describe the growth kinetics for thin oxides**
- **Experimental data show that D-G model underestimates the oxide thickness when it is less than 20 nm.**



From A.S. Grove, Physics and Technology of Semiconductor Devices, John Wiley and Sons, 1967, p. 31

Thin Oxidation Modeling

The mechanism is unknown and no model is generally accepted!

D-G: $$\frac{dx_0}{dt} = B/(2x_0 + A)$$

Model of Massoud *et al* :

$$\frac{dx_O}{dt} = \frac{B}{2x_O + A} + C\exp\left(-\frac{x_O}{L}\right)$$

$C=C^0\exp(-E_A/kT)$

$C^0 \cong 3.6\times10^8$ µm/hr

$E_A \cong 2.35$ eV

$L \cong 7$ nm

SUPREM IV use this model

… but keep in mind it is a fit for experimental data, not a Physics based simulation

Other Influences on Oxidation Rates

- Pressure
- Crystal Orientation
- Impurity
- Chlorine Doping

Effects of Pressure on Oxidation Rate

No first principles model → Deal – Grove will have to do

$$\frac{B}{A} \approx \frac{HP_G(k_S h)}{N_1(k_S + h)}$$

$$B \approx \frac{2DHP_G}{N_1}$$

Experiments have shown that in H_2O oxidation, the oxide growth rate is proportional to P_G. However, no simple linearity can be shown for dry O_2 oxidation.

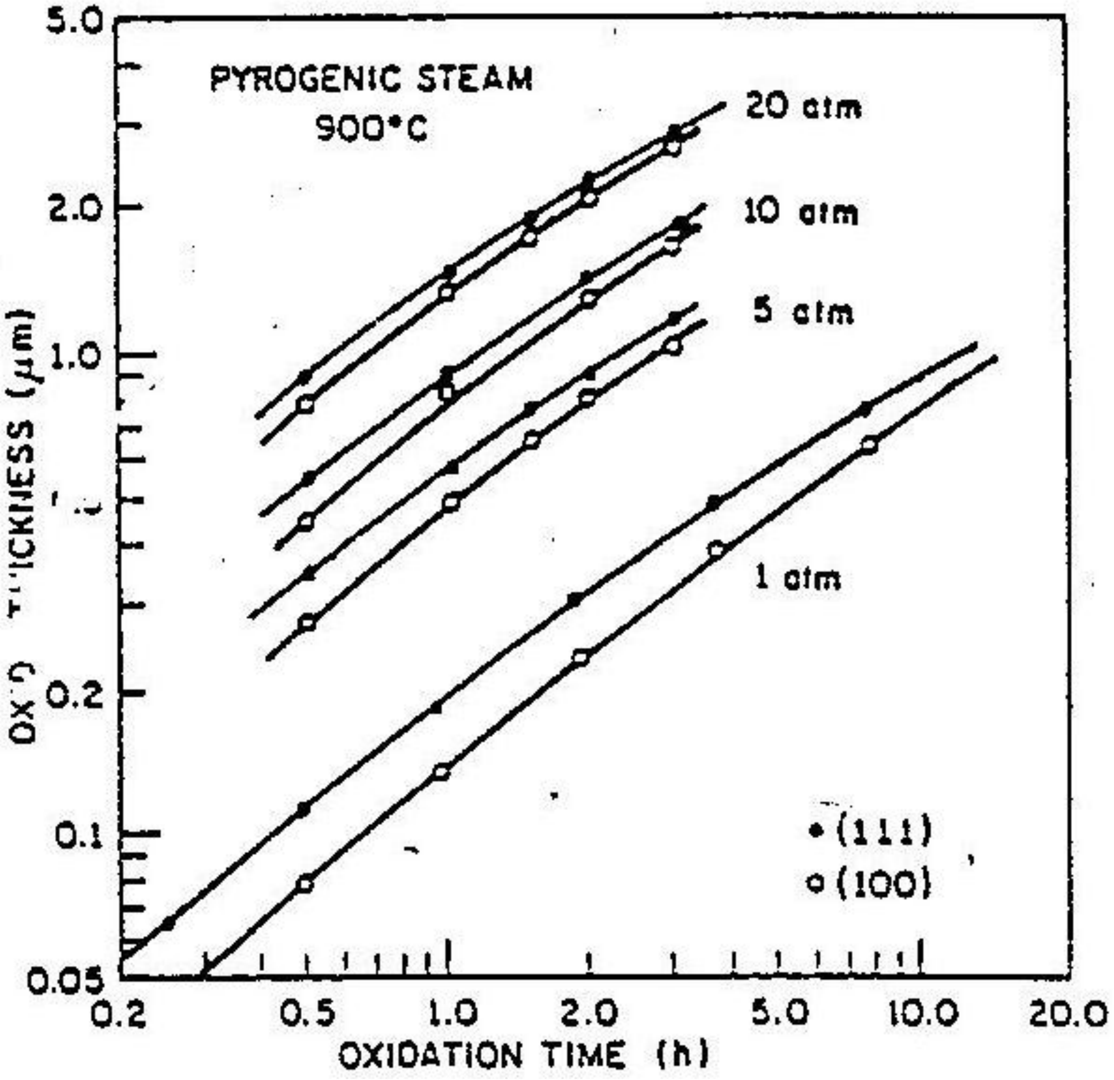
For H_2O oxidation:
$$\boxed{\begin{array}{l} \frac{B}{A} = (\frac{B}{A})^i P \\ B = (B)^i P \end{array}}$$

For dry oxidation:
$$\boxed{\begin{array}{l} \frac{B}{A} = (\frac{B}{A})^i P^n \\ B = (B)^i P \end{array}}$$

$n \cong 0.7 \sim 0.8$. The *i* superscripts refer to values at 1 atm.

1) For given growth rate, increasing pressure may decrease the oxidation temperature.
2) For given oxide thickness at fixed temperature, increasing pressure may reduce the oxidation time.

Effects of Pressure on Oxidation Rate: Steam Oxidation



Effects of Crystal Orientation on Oxidation Rate

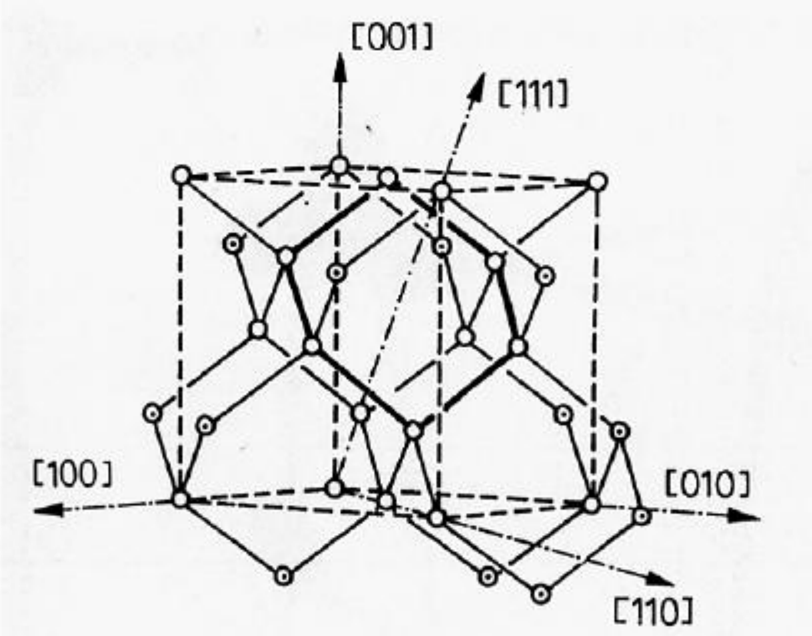
- ✓ Chemical reaction rate constant k_s depends on crystal orientation. Thus, the linear rate constant B/A is also orientation dependent:

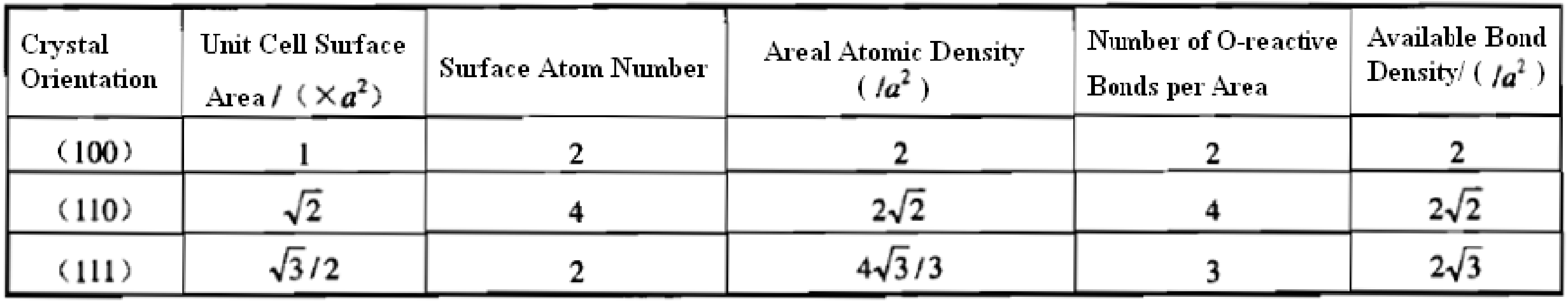
  $B/A_{(111)}=1.68\ B/A_{(100)}$

  $B/A_{(110)}=1.45\ B/A_{(100)}$

- ✓ Parabolic rate constant B is orientation independent.

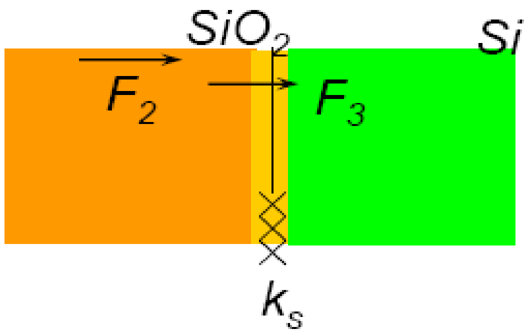
- ✓ High-temperature and long-time oxidation is dominated by B. The orientation effects are weak.





Crystal Orientation	Unit Cell Surface Area / ($\times a^2$)	Surface Atom Number	Areal Atomic Density ($/a^2$)	Number of O-reactive Bonds per Area	Available Bond Density/ ($/a^2$)
(100)	1	2	2	2	2
(110)	$\sqrt{2}$	4	$2\sqrt{2}$	4	$2\sqrt{2}$
(111)	$\sqrt{3}/2$	2	$4\sqrt{3}/3$	3	$2\sqrt{3}$

Effects of Crystal Orientation on Oxidation Rate



$$k_s = k_{s0}\exp(-E_a / kT)$$

$$E_{a(100)} > E_{a(111)} \geq E_{a(110)}$$

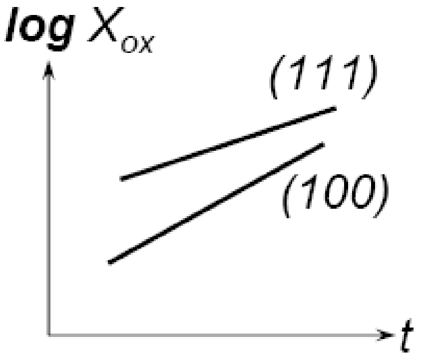
K_{s0} is constant, proportional to the number of oxidant-reactive silicon covalent bonds.

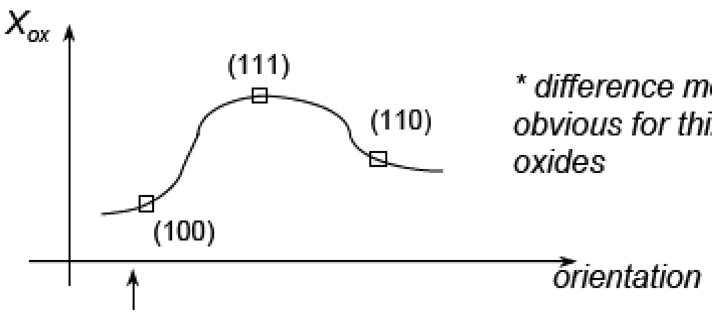
B is orientation independent

$$(B/A)_{111} = 1.68\ (B/A)_{100}$$

$k_s(111) > k_s(100)$

Crystal Orientation	Unit Cell Surface Area / ($\times a^2$)	Surface Atom Number	Areal Atomic Density ($/a^2$)	Number of O-reactive Bonds per Area	Available Bond Density/ ($/a^2$)
(100)	1	2	2	2	2
(110)	$\sqrt{2}$	4	$2\sqrt{2}$	4	$2\sqrt{2}$
(111)	$\sqrt{3}/2$	2	$4\sqrt{3}/3$	3	$2\sqrt{3}$



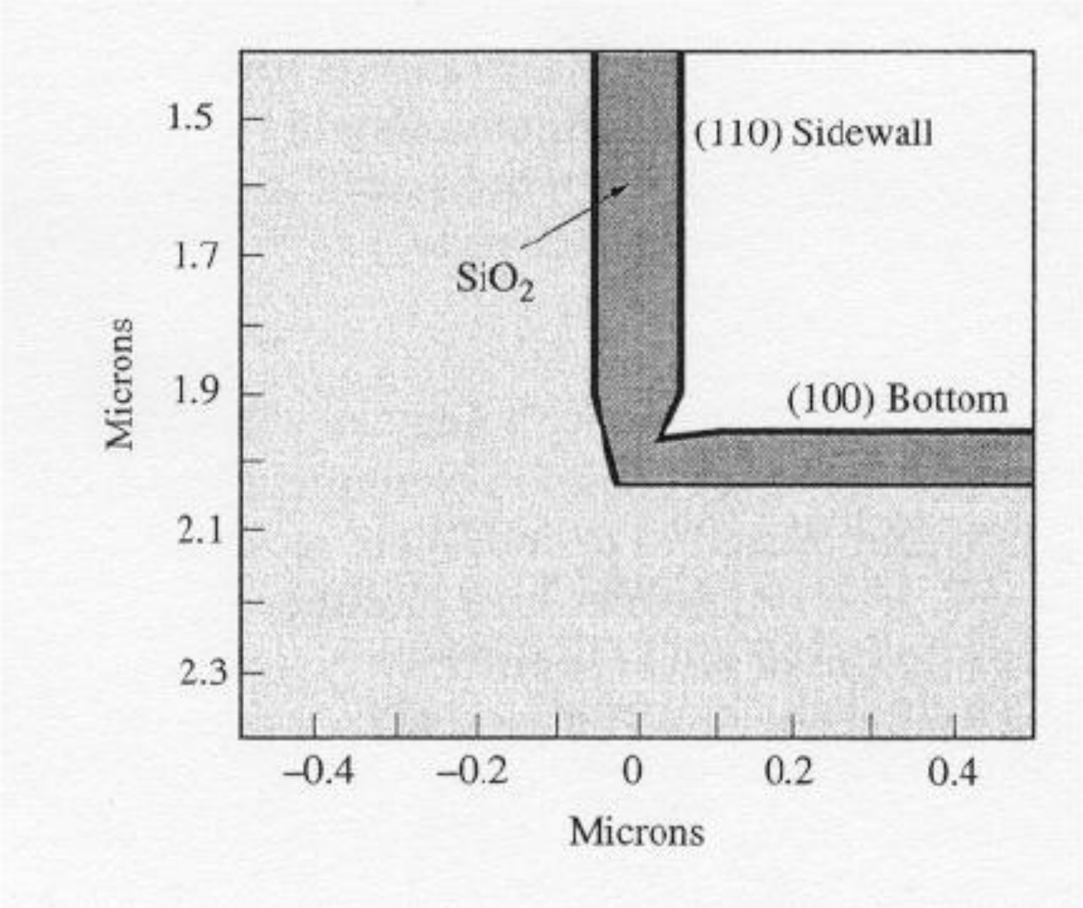


** difference more obvious for thin oxides*

most IC's made with (100) Si

Effects of Crystal Orientation on Oxidation Rate

Example: Simulation of trench oxidation using ATHENA



(100) Si,   in H_2O at 900 °C for 30 min

Effects of Impurities on Oxidation Rate

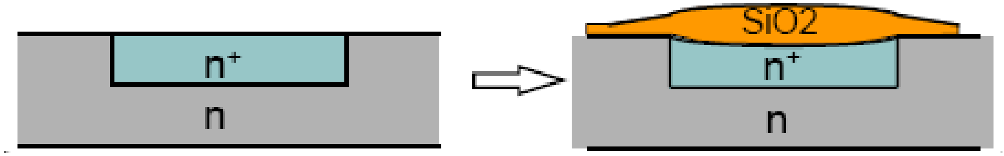
Higher oxidation rates in highly doped substrates (more pronounced for n^+)

Possibly due to vacancies V

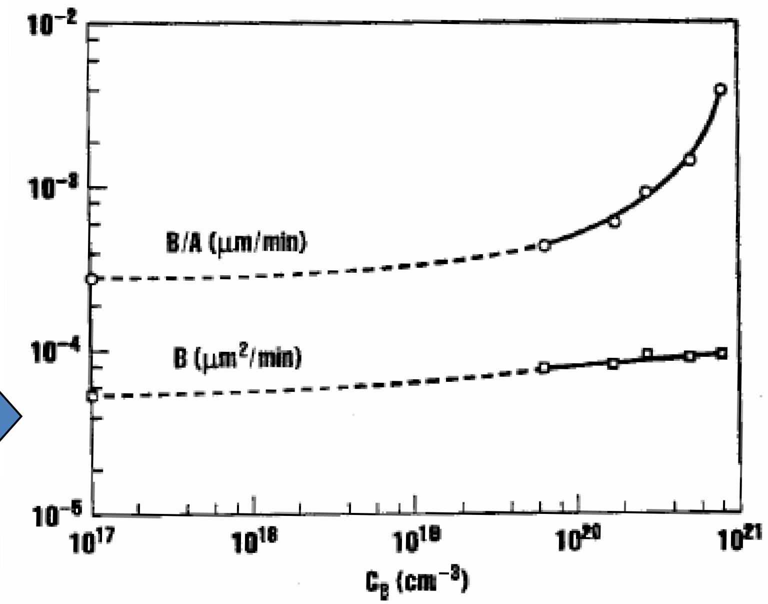
Reaction rate controlled (*B*/*A* is dominant, oxidation rate depends on the doping concentration on the silicon surface)

N-type dopants tend to segregate into Si → SiO_2 not affected by dopants → B / diffusion not affected

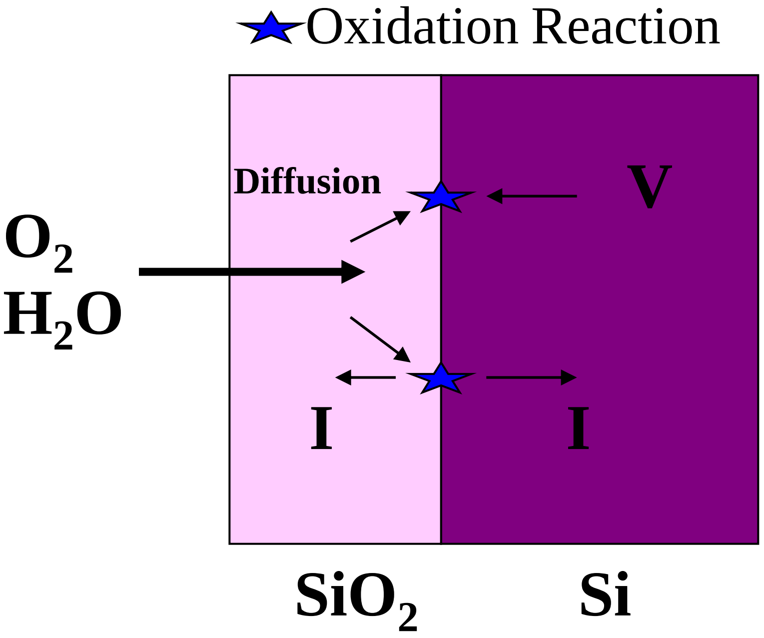
P-type dopants tend to segregate into SiO2 → parabolic rate B / Diffusion potentially affected



Dry oxidation rate varying with surface P concentration at 900 °C (Reaction rate controlled).



Effects of Impurities: Advanced Point Defect Based Model



Vacancy V :

V is much more for heavy extrinsic doping than for light doping

V is much less in p^+ doping

$$\frac{B}{A} = (\frac{B}{A})^i (1 + 2.62 \times 10^3 \exp(-\frac{1.1eV}{kT})(\frac{C_V{}^T}{C_{V_i}{}^T} - 1)$$

$C_V{}^T$: Total Vacancy Concentration

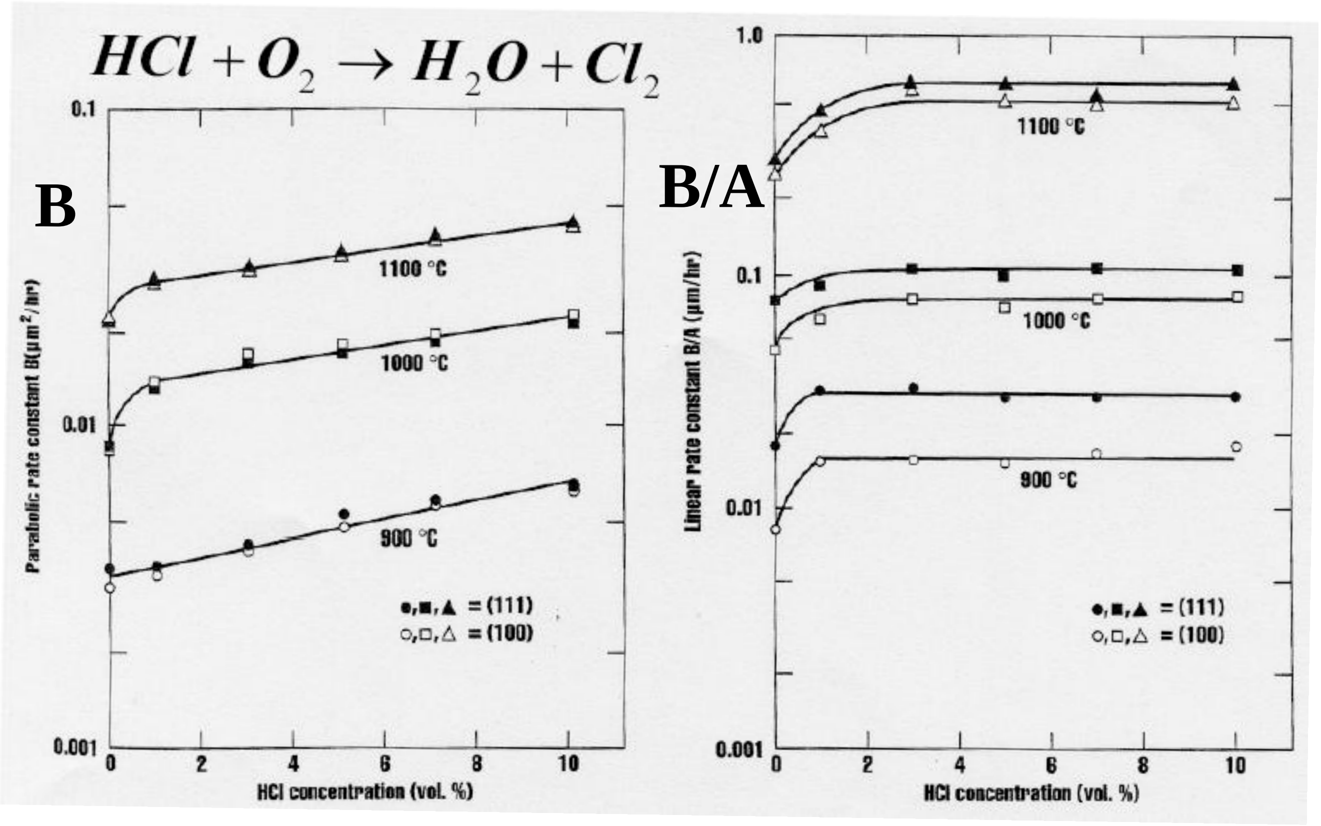
$C_{Vi}{}^T$: Total Vacancy Conc. in intrinsic material

$$(1+2\gamma)\ \mathrm{Si} + 2\mathrm{O_I} + 2\beta \mathrm{V} \leftrightarrow \mathrm{SiO_2} + 2\gamma \mathrm{I} + \mathrm{Stress}$$

γ, δ: fraction of interstitials, vacancies contributing to the oxidation process

Effects of Chlorine Doping on Oxidation Rate

- Cl_2 can increase B/A and B. The bond energy of Si-O is 4.25 eV, and that of Si-Cl is 0.5 eV. Cl_2 reacts with Si to generate $SiCl_4$, which reacts with oxygen to get SiO_2. So Cl_2 is catalyst.
- Cl^- can also neutralize accumulated interface charges



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

Dry O_2 + 1-3% Cl; Cl is a metal getter ⇒ cleaner oxide.

Lecture 5: Concept Test 5.1

- **5.1: Which of the following statements are true?**

A: Mass-transport, diffusion and interface reactions play important roles in oxidation kinetics.

B: The gas pressure in the oxidation furnace affects the parabolic rate constant, but not the linear rate const.

C: The Deal-Grove model could be applied to Silicon Epitaxy

D: H_2O tends to oxidize faster because of a higher surface reaction constant compared to O_2

E: None of the above

Lecture 5: Concept Test 5.1

- **5.1: Which of the following statements are true?**

A: Mass transport, diffusion and interface reactions play important roles in oxidation kinetics.

No, mass transport is negligible

B: The gas pressure in the oxidation furnace affects the parabolic rate constant, but not the linear rate const.

No, it affects both, because P_g~C_g, sub-linear for O_2

C: The Deal-Grove model could be applied to Silicon Epitaxy

No, mass transport eliminated from D-G

D: H_2O tends to oxidize faster because of a higher surface reaction constant compared to O_2

No, ~1000 x higher solubility enhances oxidation rate (C*)

E: None of the above

Summary: Relations of B/A and B to Process Parameters

	Linear Rate Constant *B*/*A*	Parabolic Rate Constant *B*
Pressure (H_2O Oxidation)	**linear**	**linear**
Pressure (Dry Oxidation)	**Sub-linear**	**linear**
H_2O *vs.* Dry (Oxidation)	**higher rate in H_2O**	**higher rate in H_2O**
Si Crystal Orientation	$B/A_{(111)}:B/A_{(100)}=1.68:1$	**independent**
Si Doping Concentration (C)	**Increasing with C**	**weak dependence**
Chlorine Doping	**Increased**	**Increased**

Summary of Key Notes

1. Which factors influence the oxidation rate?
2. What is relationship between oxidation rate and pressure?

Pressure, Crystal Orientation, Doping Concentration, Chlorine
The more pressure, the faster oxidation rate. H_2O oxidation is linear with pressure while dry oxidation is exponential.

3. Which silicon crystal orientation has the fastest oxidation rate? Which one has the slowest rate? Why?

(111) has the fastest oxidation rate while (100) has the slowest one. k_s is related to the activation energy and silicon covalent bond density. B is independent of orientation. For thick oxide, the effect of orientation is very weak.

4. For very thin oxide, how does the calculated thickness based on the Deal-Grove model differ from the actual one? How to correct?

For dry oxidation when the oxide is less than 20 nm thick, the thickness calculated based on D-G model is much less than the actual one. Correction: add an item which decays exponentially with the increasing thickness.

5. What are the effects of chlorine doping on the oxide films?

Chlorine doping can increase the reaction rate, reduce fixed charges at interface and interface states (charge neutralization), and getter alkali ions.

Thermal Oxidation of Silicon: Outline

- Applications
- Properties and fabrication
- Linear parabolic model (Deal-Grove Model)
- Extensions of model
- **Defects in SiO_2**
- Characterization (recap from Lecture 4)

Si/SiO$_2$ Interface Properties

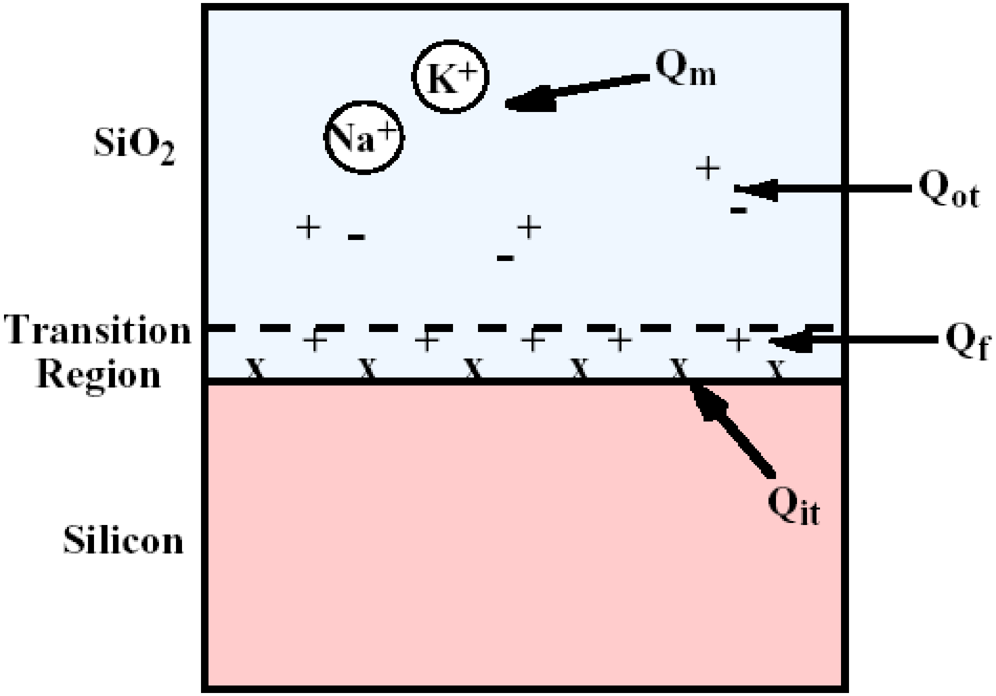
1) Fixed Oxide Charge, Q_f

2) Interface trapped charge, Q_{it}

3) Mobile ionic charge, Q_m

4) Oxide trapped charge, Q_{ot}

From Deal



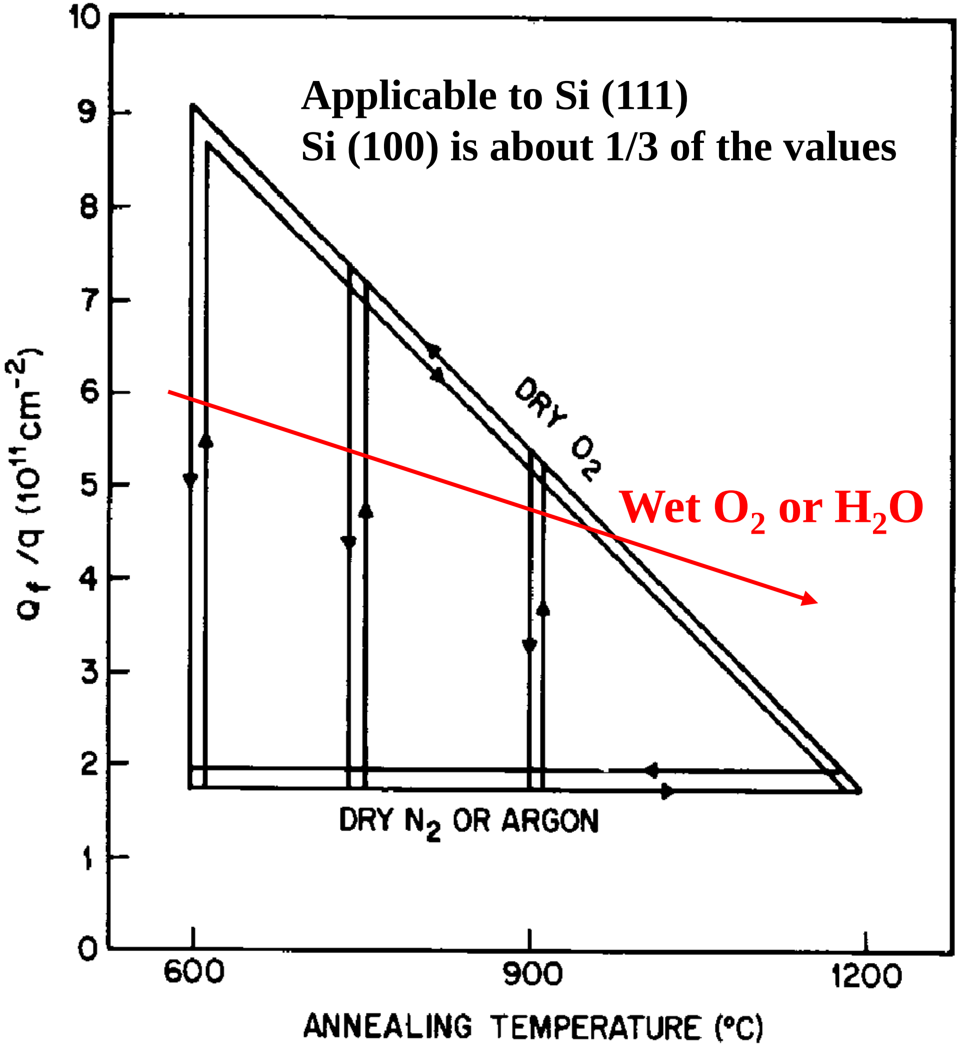
Si/SiO$_2$ Interface Properties: Fixed Oxide Charge, Q_f

- Position: Within 2～3 nm of the interface
- Positive Charge. Charge density: 10^9-10^{11} cm^{-2}. Charge state does not change during normal device operation.
- Suggested origin: Incompletely oxidized Si atoms having a net positive charge.

≡Si·

- Q_f decreases with increasing temperature
- The faster speed of cooling down, the lower value of Q_f. But wafers with diameter>100 mm cannot be cooled too fast.
- Q_f<111>:Q_f<110>:Q_f<100>=3:2:1
- Reproducible

Si/SiO_2 Interface Properties: Fixed Oxide Charge, Q_f



Deal Q_f Triangle

Hypotenuse represents the relationship between temperature and Q_f
The higher temperature, the lower Q_f.

The vertical edge means that with constant oxidation temperature, Q_f can be reduced quite much by changing the ambient (N_2 or Ar)

The horizontal edge represents the cooling process in inert gases

Si/SiO$_2$ Interface Properties: Interface Trapped Charge, Q_{it}

Position: at Si/SiO$_2$ interface

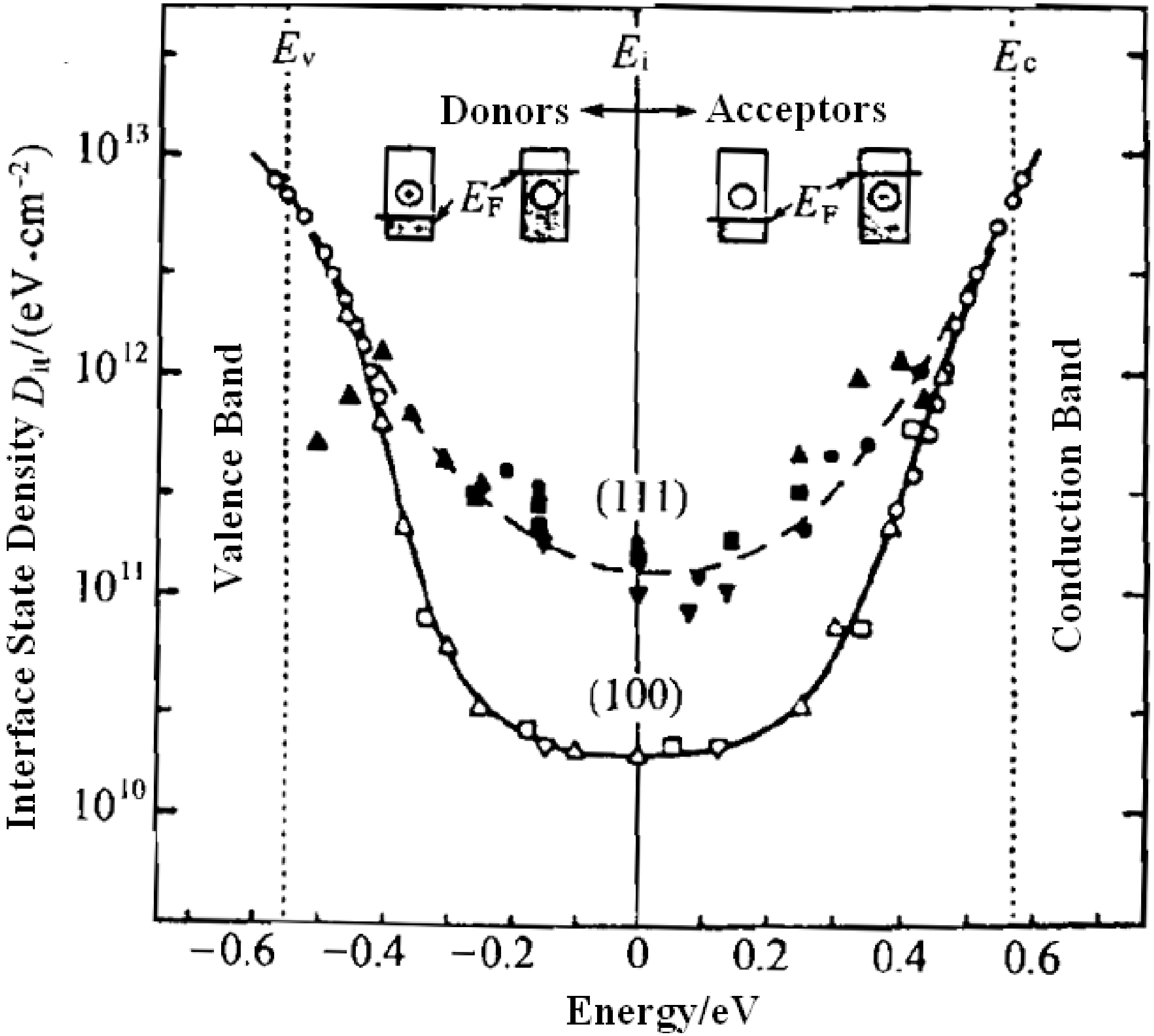
Suggested origin:

1) Dangling bonds located in the oxide
2) ≡Si·
3) Ionized impurities (traps), can bind interface carriers

Charge: Energy exists throughout the forbidden band. Q_{it} can exchange charge with silicon. Depending on bias, Q_{it} may be positive, neutral or negative. Density:10^9-10^{11} $cm^{-2}eV^{-1}$

Q_{it} has the same origin as Q_f: high-value Q_f results in high-value Q_{it}

Si/SiO$_2$ Interface Properties: Interface Trapped Charge, Q_{it}

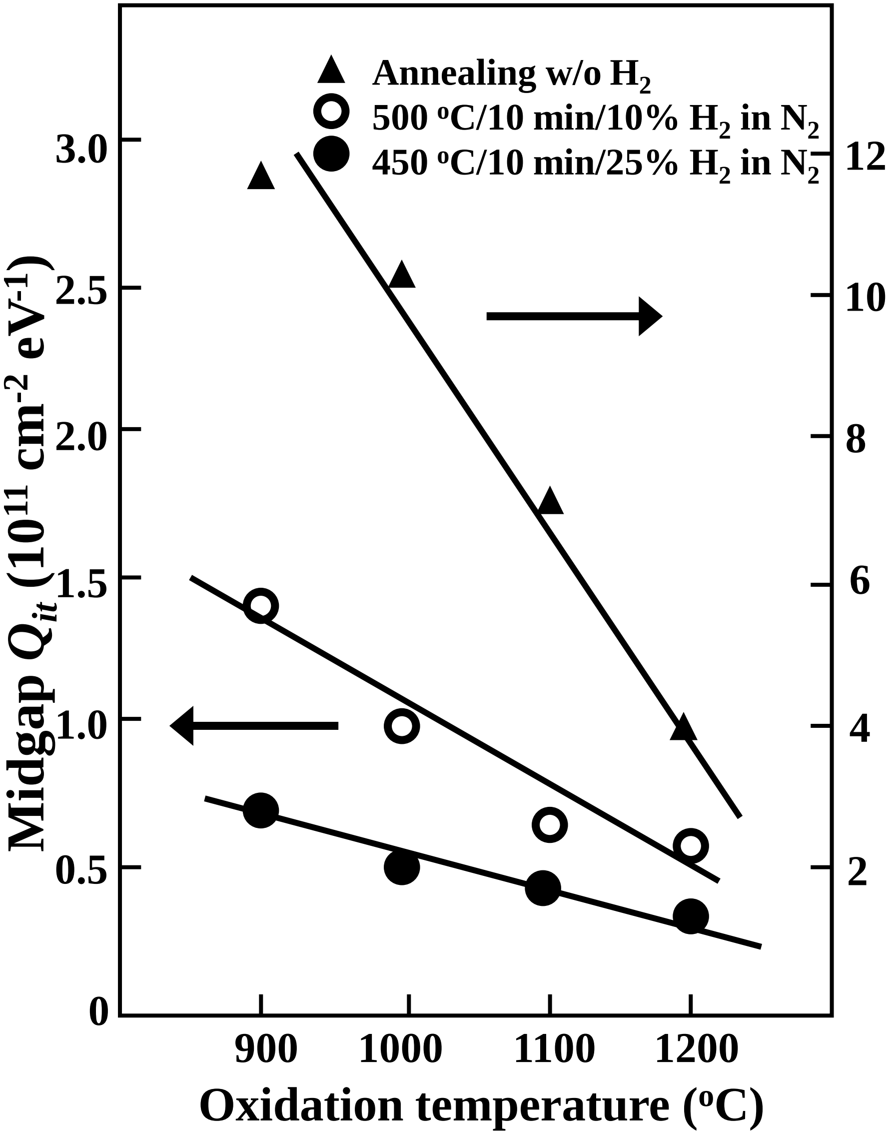


Si/SiO_2 Interface Properties: Interface Trapped Charge, Q_{it}

- ☐ Q_{it} relates to:
  Oxidation temperature, oxidation ambient (wet O2, dry O2), and crystal orientation, etc.
- ☐ Relation between Q_{it} and dry oxidation temperature
- 1) Q_{it} decrease with increasing temperature
  2) At the middle of the band, $Q_{it(100)}$ is 5 times lower than $Q_{it(111)}$

- ☐ Method to reduce Q_{it}
  Low Temperature Post-Metallization Anneal (PMA)
  Anneal at H_2 (or H_2-N_2) (Forming Gas Annealing, FGA) or Ar at 350-500 °C for 30 min
  - Before annealing, $Q_{it} \sim 10^{11}$ cm^{-2}eV^{-1}
  - After annealing, $Q_{it} \sim 10^{10}$ cm^{-2}eV^{-1}, useful!

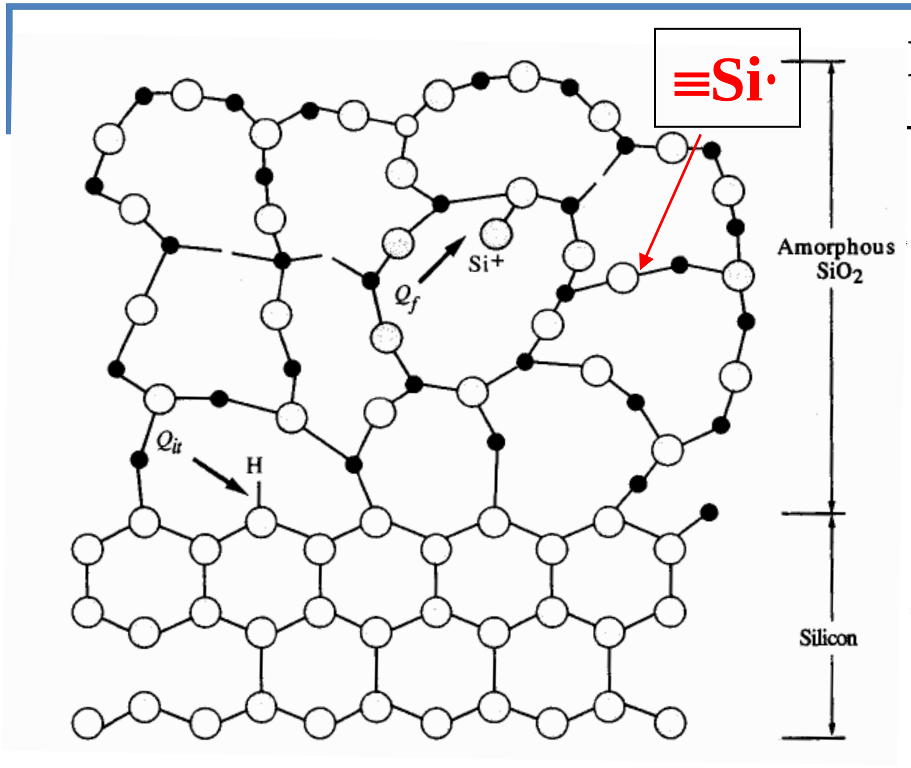
Si/SiO$_2$ Interface Properties: Interface Trapped Charge, Q_{it}

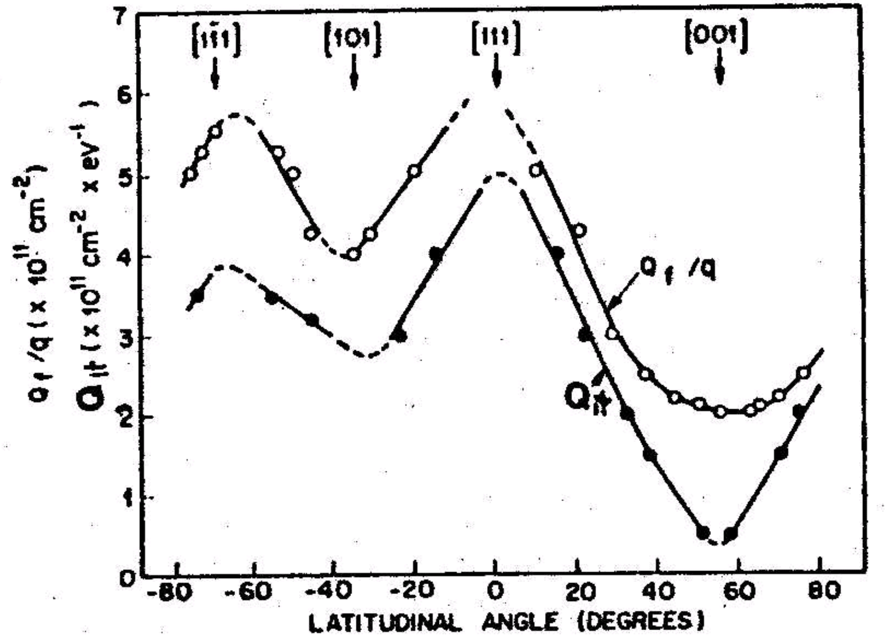


Examples for effective reduction of Q_{it} by FGA

Dependence of Q_f and Q_{it} on Orientation

—— (100) has the lowest value





Chlorine doping oxidation

Low-Temperature Alloy Anneal (H2 passivation)

High-Temperature Argon Anneal

Q_{it} & Q_f :

- ✓Decrease with temperature
- ✓Increase with interface roughness
- ✓Much smaller in <100> than in <111>

Si/SiO_2 Interface Properties: Mobile Ionic Charge, Q_m

- ☐ Position: Anywhere in the oxide. Q_m originally locates at gate (metal/poly-Si)/SiO_2 interfaces. But under positive bias or elevated temperature, it moves towards Si/SiO_2 interfaces.
- ☐ Origin: Metallization and other contaminations
- ☐ Caused by alkali inos (Na^+, K^+) contamination (existing in the form of network modifier)
- ☐ Change the threshold voltage V_T of MOS devices and reduce their stability.

Si/SiO$_2$ Interface Properties: Mobile Ionic Charge, Q_m

Methods to reduce Q_m

1) Clean quartz tube by O_2-HCl gas at 1150 °C/2 h

2) Use Chlorine doping oxidation. Chlorine sources can be HCl-O_2, TCE, TCA and so on.

3) Use Phosphosilicate glass (PSG)

4) Use Si_3N_4 as the final passivation layer

Not an issue anymore!

Si/SiO$_2$ Interface Properties: Oxide Trapped Charge, Q_{ot}

❖ Position: Anywhere in oxide. For example, when X ray enters SiO$_2$, electron-hole pairs are generated and trapped by defects in oxide.

❖ Origin: broken bonds, such as Si-O、Si-Si、Si-H、Si-OH

- ionization irradiation

- VLSI processes, such as e-beam evaporation, sputtering, plasma etching, e-beam or x-ray lithography, and ion implanation.

❖ As a result, these traps will capture electrons or holes and they will be injected into the oxide during device operation.

◆1000 °C dry oxidation can improve SiO$_2$ structure and make them not easy to break

——Anti-radiation oxidation

◆Anneal in H$_2$ or inert ambient at 300 °C

◆Add radiation-insensitive passivation layers, such as Al$_2$O$_3$ and Si$_3$N$_4$

Thermal Oxidation of Silicon: Outline

- Applications
- Properties and fabrication
- Linear parabolic model (Deal-Grove Model)
- Extensions of model
- Defects in SiO_2
- **Characterization (recap from Lecture 4)**

Quality Inspection of Silicon Oxide

1. Detect Defects in Oxide Film

- 1) Detect Pores in Oxide Film

  EPW (Ethylenediamine－Pyrocatechin－Water Etching)

  Anodic Oxidation

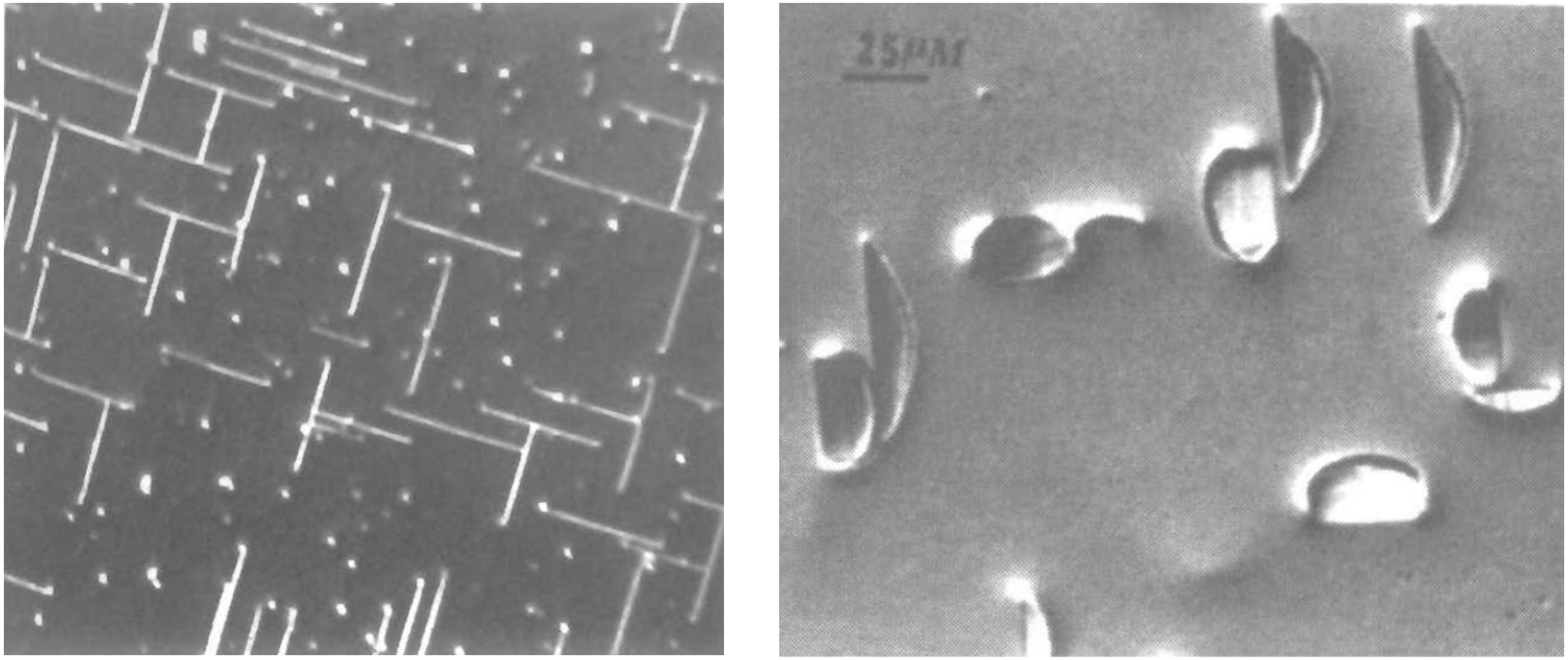
  Chlorine Etching

  MOS Diode Method
- 2) Detect Oxidation induced stacking faults (OISF)

  After oxidation, remove SiO_2 by HF and etch it using Sirtl solution

  Sirtl solution: 100 ml H_2O + 50 g Cr_2O_3 +75 ml HF
- 3) Measure Na^+ concentration in oxide films (see Chapter 6.4.3 Electrical Measurements: Bias Temperature Stressing, BTS)

Example: OISF – Oxidation Induced Stacking Fault

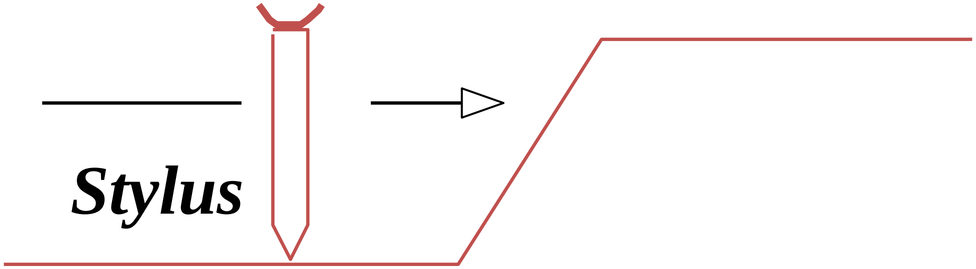


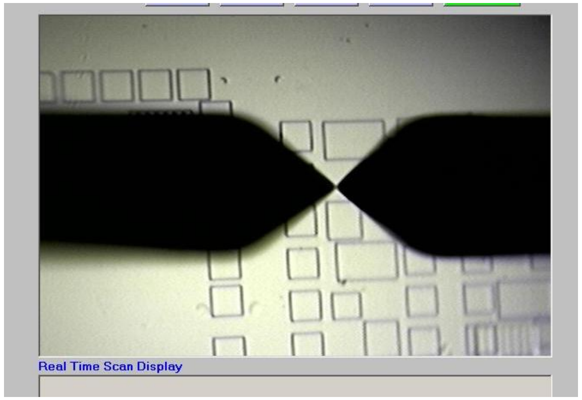
Oxidation generates a lot of interstitial atoms. These point defects gather to form large 2D defects——Stacking Fault. Stacking faults, locating at the interface, are trap sites for gettering and may cause increased leakage current. High-pressure (low temperature) oxidation and chlorine doping oxidation can effectively suppress OISF。

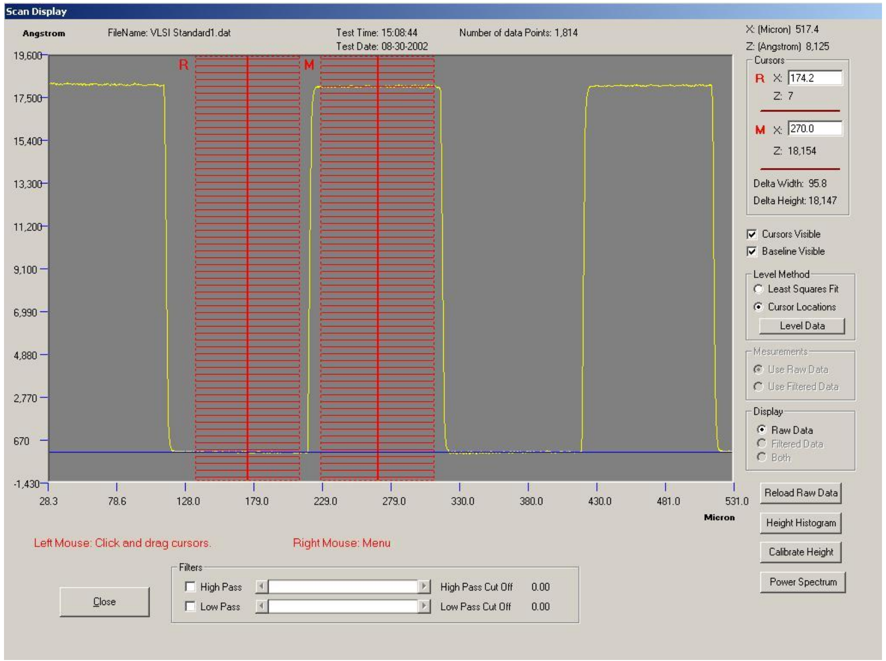
Metrology: Thickness Measurements

Mechanics: Step Profiler

- **Mechanics**
- **Colorimetry**
- **Ellipsometry**
- **Interferometry**
- **C-V Measurement**
- **Determine Weight**







FileName: VLSI Standard1.dat

Test Time: 15:08:44
Test Date: 08-30-2002

Number of data Points: 1,814

X: (Micron) 517.4
Z: (Angstrom) 8,125

Cursors
R X: 174.2
Z: 7
M X: 270.0
Z: 18,154
Delta Width: 95.8
Delta Height: 18,147

☑ Cursors Visible
☑ Baseline Visible

Level Method
○ Least Squares Fit
● Cursor Locations

Mesurements
● Use Raw Data
○ Use Filtered Data

Display
● Raw Data
○ Filtered Data
○ Both

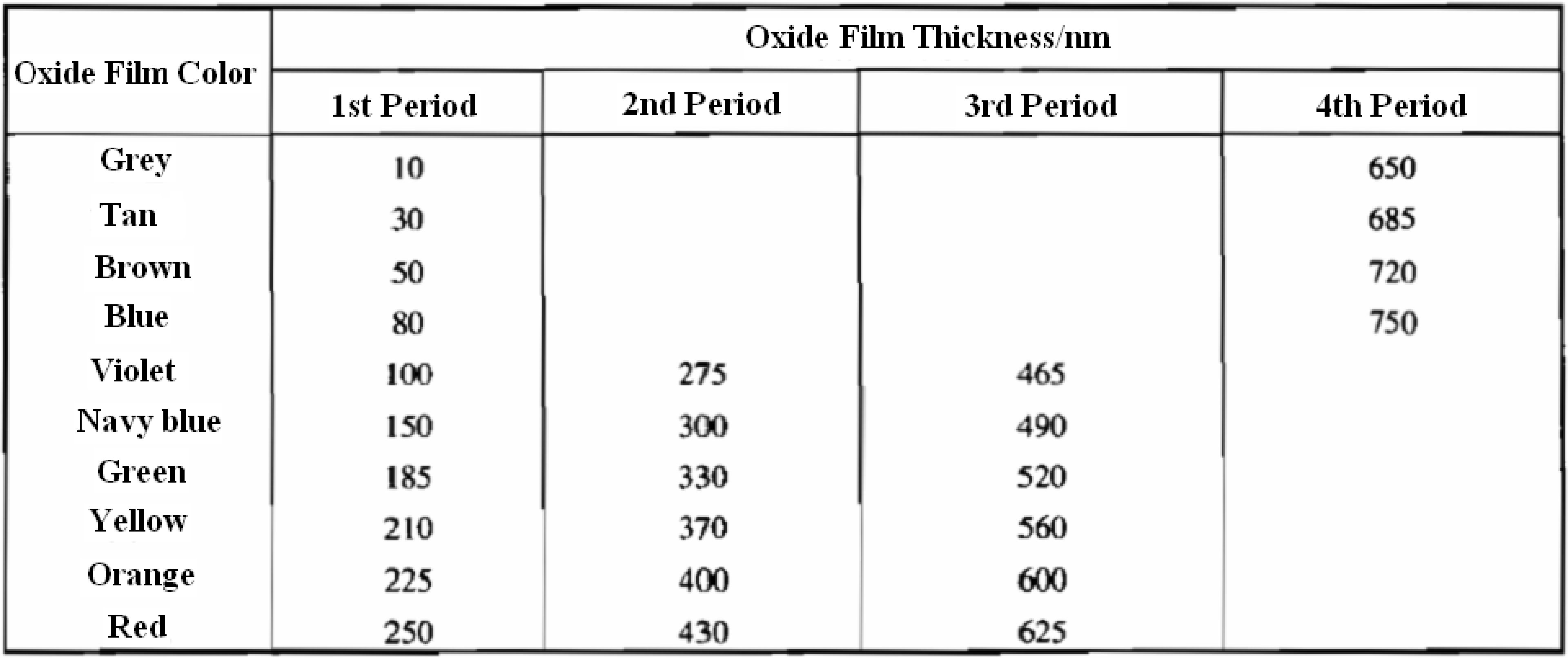
Left Mouse: Click and drag cursors.

Right Mouse: Menu

Filters
☐ High Pass — High Pass Cut Off 0.00
☐ Low Pass — Low Pass Cut Off 0.00

Metrology: Thickness Measurements

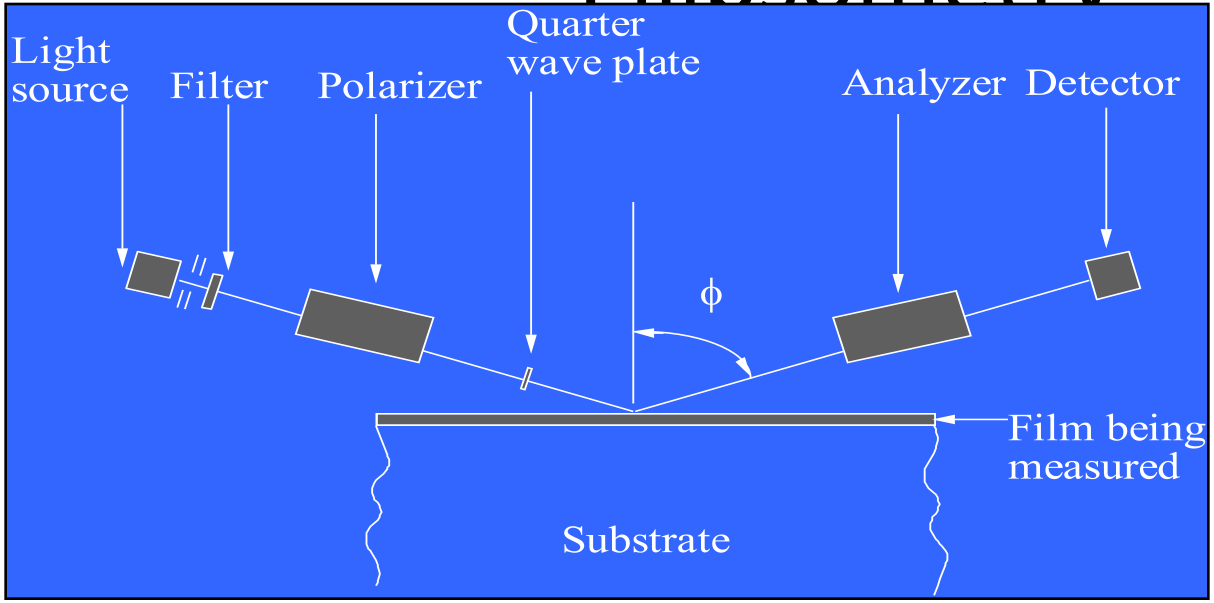
Colorimetry

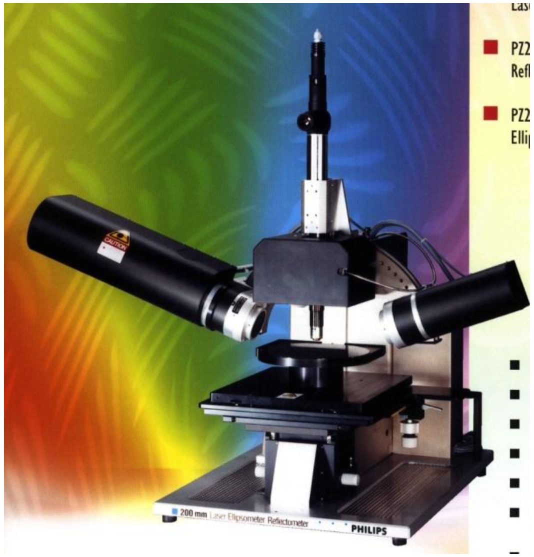


Oxide Film Color	Oxide Film Thickness/nm			
	1st Period	2nd Period	3rd Period	4th Period
Grey	10			650
Tan	30			685
Brown	50			720
Blue	80			750
Violet	100	275	465	
Navy blue	150	300	490	
Green	185	330	520	
Yellow	210	370	560	
Orange	225	400	600	
Red	250	430	625	

Metrology: Thickness Measurements

Ellipsometry





Monochromatic light becomes polarized after passing through polarizer, turns into elliptical polarized light by quarter wave plate and then arrives at the samples. After film reflection and analyzer, it turns into monochromatic light and enters the phototube acceptor.

The amplitude and phase changes of the components of two perpendicular polarized light are dependent of film thickness and refractive index.

Today: Spectroscopic Ellipsometry (Installed in Electrum in Feb. 2011)

Metrology: Thickness Measurements
Ellipsometry: accurate, flexible, non-destructive

Thickness measurement:

- Measurements provide periodic thickness

- Require to know some properties of the film

- Multi-wavelength measurement

Thickness and refractive index:

- Can determine the thickness of different materials and their refractive indexes

Multi-layer film:

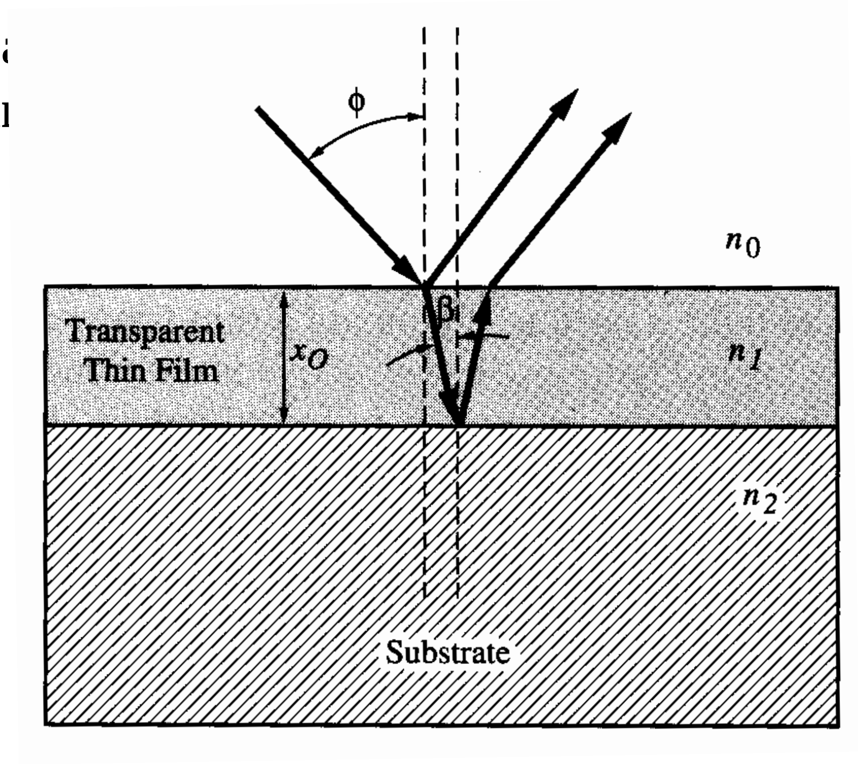
- Can use multi-wavelength and multi-angle to determine the thickness of multi-layer films

Metrology: Thickness Measurements

Interferometry

- According to optical coherence, the light reflecting from the thin film surface interferes with that from the film/substrate interface. When the optical path difference is integra length (the intensity will i thickne

$$x_0 = m\frac{\lambda}{2n}$$



n: Refractive index of SiO_2

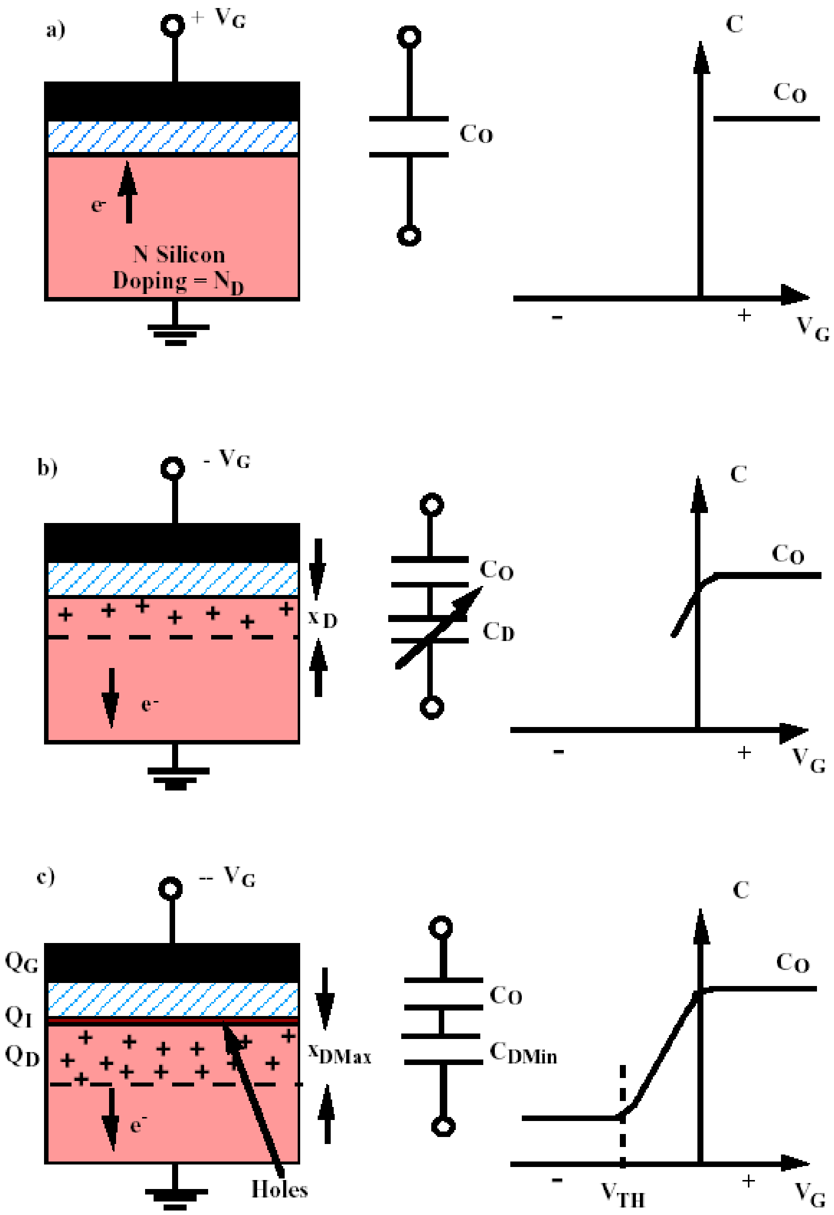
λ: Wave length of incident light, e.g., λ = 589.6 nm

m: Interference fringe number

Thickness Measurements

Electrical Measurement

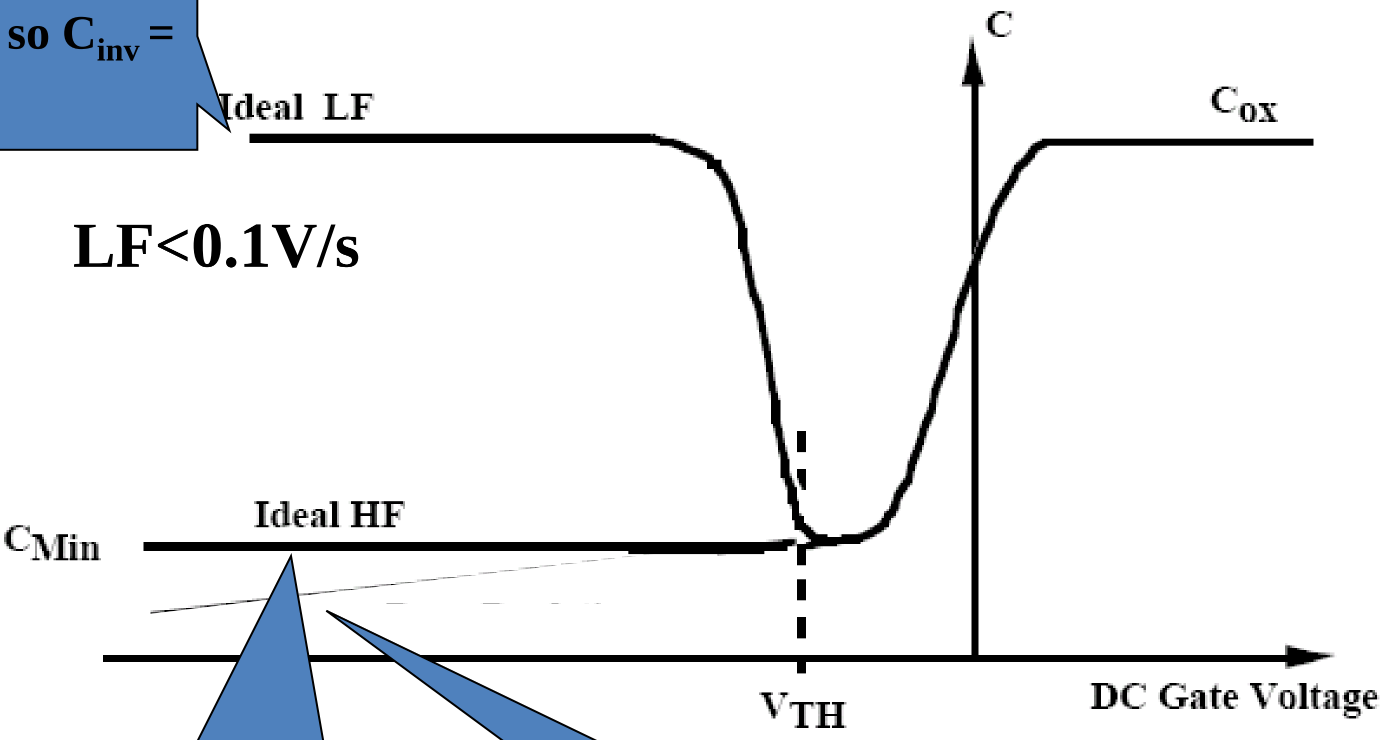
- (a) Positive voltage is applied at the metal electrodes (accumulation)
- (b) Negative voltage induces depletion in the substrate
- (c) Further more negative voltage results in inversion



At low frequency, Q_I completely balances gate charge. so C_{inv} = C_{ox}

$$Q_G = qN_D x_D + Q_I$$

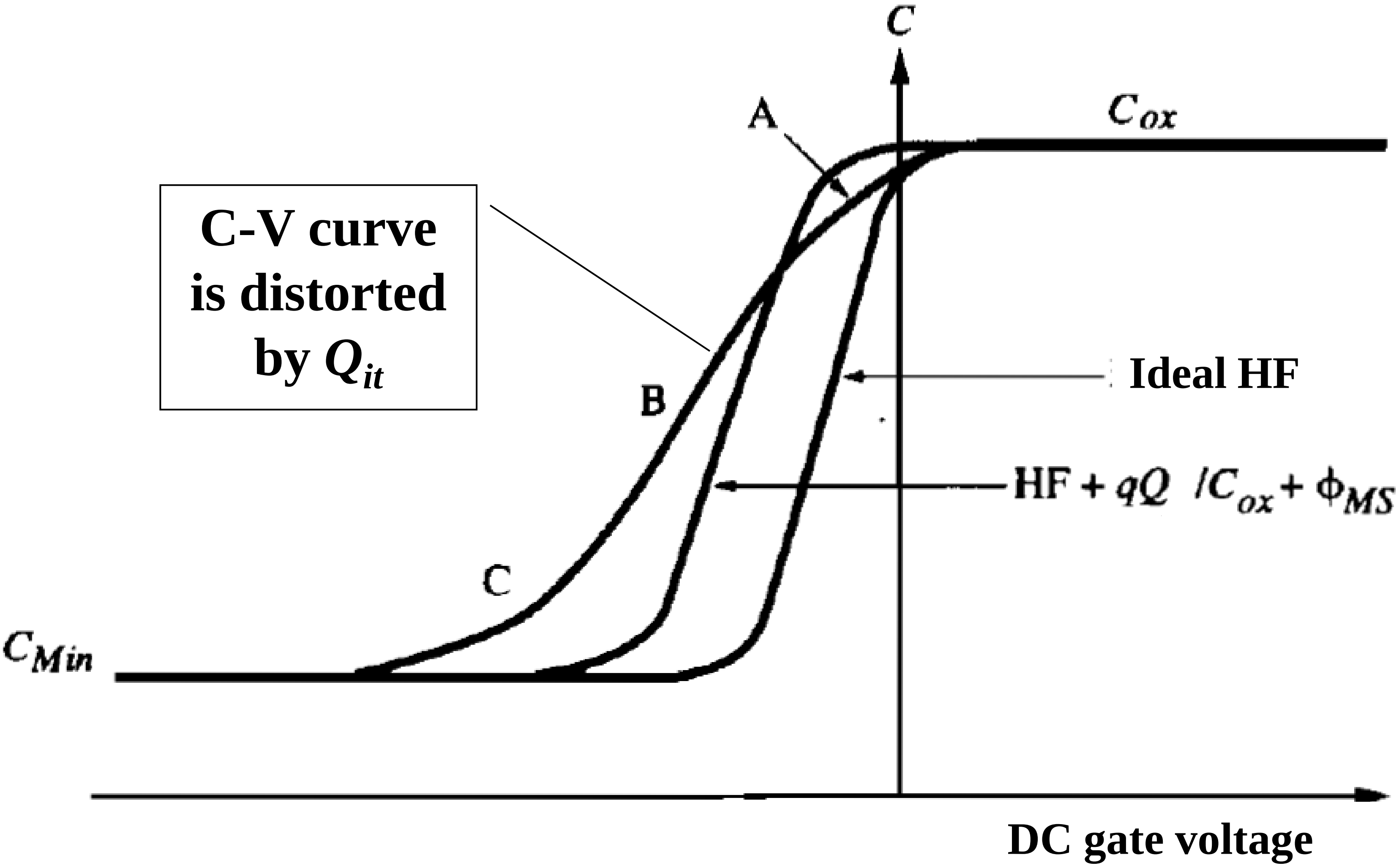
LF<0.1V/s



At high frequency, Q_I cannot follow the frequency change. C_{inv} is the series connection of C_{ox} and C_D.

Deep depletion: at high frequency, x_D is added to balance gate charge.

C-V Curves: Effects of Interface Charge on MOS Capacitor



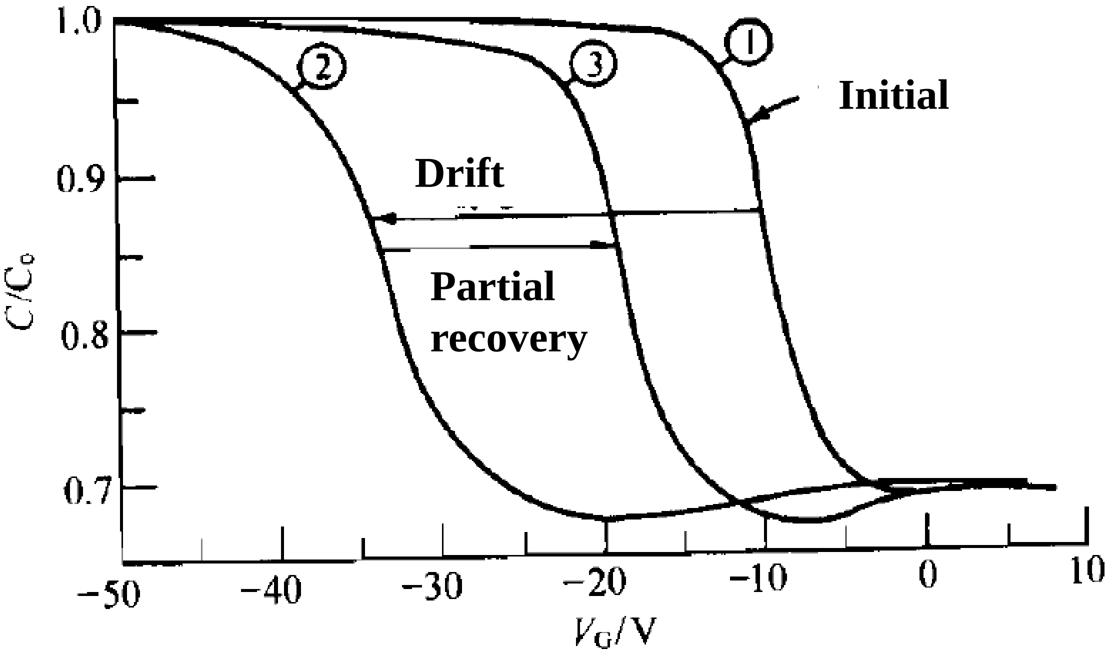
C-V curve is distorted by Q_{it}

Measure Mobile Ions (Na+) Concentration in Oxide (B-T)

1. First-time C-V measurement ①.

2. Apply about 1 MV/cm positive bias on the gate and heat the device to 200-300 °C. Keep the gate voltage for 10-30 min at elevated temperature to make all the mobile ions move to the Si/SiO$_2$ interface. Keep the bias and cool the device down to room temperature. Second-time C-V measurement ②.

3. Repeat Step 2 with negative gate bias. Third-time C-V measurement ③.



$$N_{m\,total} = \frac{C_{ox}\Delta V_{FB\,\max}}{q}$$

$$N_{m\,move} = \frac{C_{ox}\Delta V_{FB}}{q}$$

Summary of Thermal Oxidation

✓Thermal oxidation is a key process of CMOS technology, especially gate oxidation, whose thickness should be controlled at atomic level. Thermal oxidation mainly applies to gate/tunneling dielectrics, mask and field oxidation.

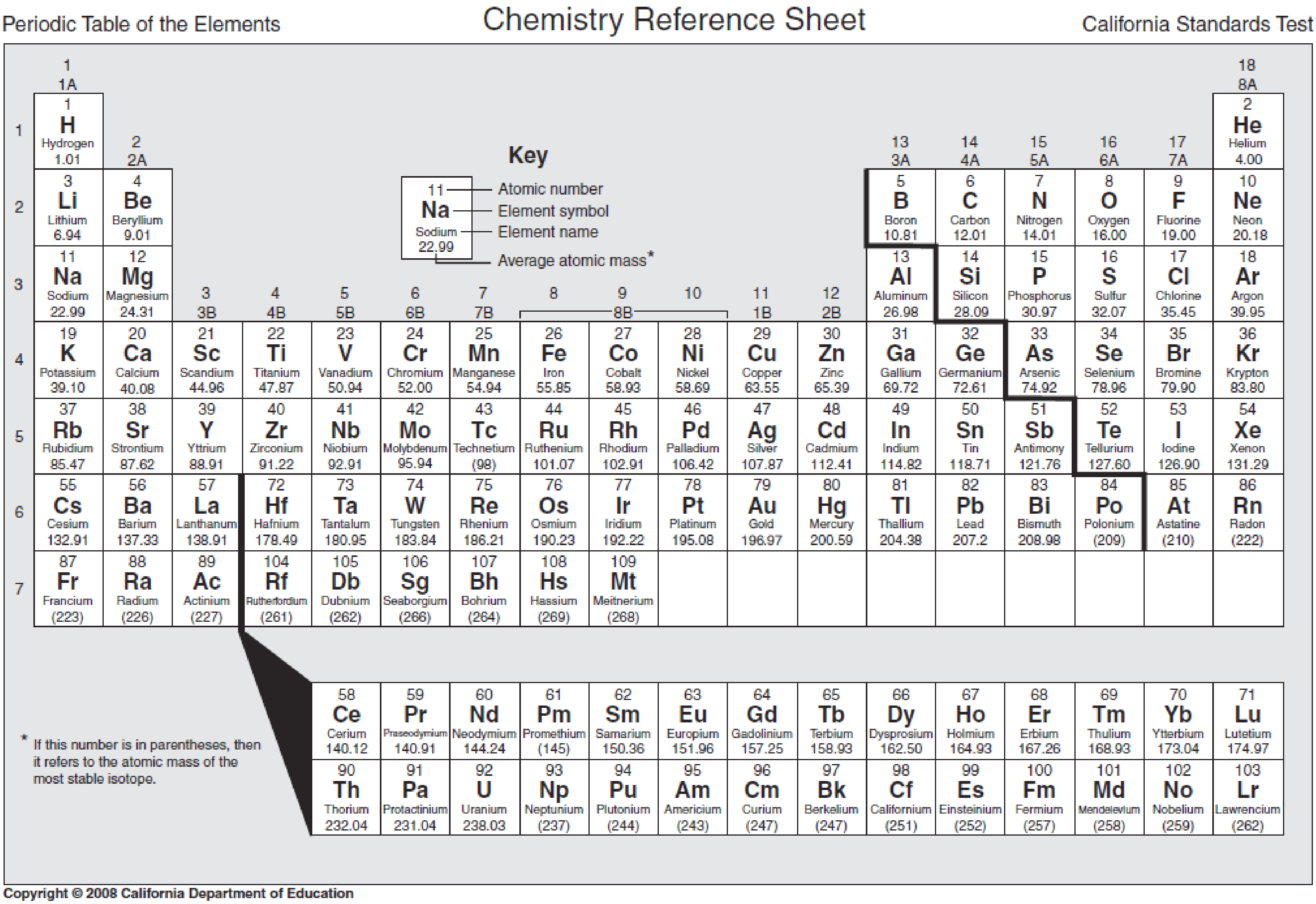
✓The mechanism of thermal oxidation is that oxidant diffuses in oxide and reacts at interface. Silicon oxide grows at the interface and consumes bulk silicon. There are dry O_2 oxidation, wet O_2 oxidation and H_2O oxidation.

✓D-G (Linear－Parabolic) model and its correction—— the meanings of *B* and *B*/*A* and the model applications

✓Dependence on oxidation rate: Pressure, Impurity concentration, Crystal orientation, Chlorine doping. Impurity redistribution.

✓Si/SiO_2 interface has much better property than any other semiconductor/ insulator interface. (100) has the best interface property. Interface charge (Q_f, Q_{it}, Q_m, Q_{ot}) may be measured by MOS C-V measurement.

✓Non-planar oxidation is affected by crystal orientation, 2D diffusion in shaped oxide and stress. Stress reduces k_s and D and hence decrease oxidation rate at corners and shaped regions.



Periodic Table of the Elements

Chemistry Reference Sheet

California Standards Test

	1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1	1 **H** Hydrogen 1.01																	2 **He** Helium 4.00
2	3 **Li** Lithium 6.94	4 **Be** Beryllium 9.01											5 **B** Boron 10.81	6 **C** Carbon 12.01	7 **N** Nitrogen 14.01	8 **O** Oxygen 16.00	9 **F** Fluorine 19.00	10 **Ne** Neon 20.18
3	11 **Na** Sodium 22.99	12 **Mg** Magnesium 24.31											13 **Al** Aluminum 26.98	14 **Si** Silicon 28.09	15 **P** Phosphorus 30.97	16 **S** Sulfur 32.07	17 **Cl** Chlorine 35.45	18 **Ar** Argon 39.95
4	19 **K** Potassium 39.10	20 **Ca** Calcium 40.08	21 **Sc** Scandium 44.96	22 **Ti** Titanium 47.87	23 **V** Vanadium 50.94	24 **Cr** Chromium 52.00	25 **Mn** Manganese 54.94	26 **Fe** Iron 55.85	27 **Co** Cobalt 58.93	28 **Ni** Nickel 58.69	29 **Cu** Copper 63.55	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.72	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.92	34 **Se** Selenium 78.96	35 **Br** Bromine 79.90	36 **Kr** Krypton 83.80
5	37 **Rb** Rubidium 85.47	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.91	40 **Zr** Zirconium 91.22	41 **Nb** Niobium 92.91	42 **Mo** Molybdenum 95.94	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.91	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.87	48 **Cd** Cadmium 112.41	49 **In** Indium 114.82	50 **Sn** Tin 118.71	51 **Sb** Antimony 121.76	52 **Te** Tellurium 127.60	53 **I** Iodine 126.90	54 **Xe** Xenon 131.29
6	55 **Cs** Cesium 132.91	56 **Ba** Barium 137.33	57 **La** Lanthanum 138.91	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.95	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.21	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.22	78 **Pt** Platinum 195.08	79 **Au** Gold 196.97	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.38	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.98	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)
7	87 **Fr** Francium (223)	88 **Ra** Radium (226)	89 **Ac** Actinium (227)	104 **Rf** Rutherfordium (261)	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (266)	107 **Bh** Bohrium (264)	108 **Hs** Hassium (269)	109 **Mt** Meitnerium (268)									

Key

11 — Atomic number
Na — Element symbol
Sodium — Element name
22.99 — Average atomic mass*

58 **Ce** Cerium 140.12	59 **Pr** Praseodymium 140.91	60 **Nd** Neodymium 144.24	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.96	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.93	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.93	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.93	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.97
90 **Th** Thorium 232.04	91 **Pa** Protactinium 231.04	92 **U** Uranium 238.03	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (262)

* If this number is in parentheses, then it refers to the atomic mass of the most stable isotope.

Taken from: http://www.sciencegeek.net/tables/CA_CST.pdf