

FYS4310

Oxidation

(Cambell chapter 4)

Fys4310 Oxidation, Overview

What is Oxidation used for?

Surface passivation, Isolation, -to conductors,
- between conductors, - **gate oxide, field oxide**
Diffusion mask, Implantation mask,

Oxidation techniques

Thermal oxidation

Wet, Dry, HCl, TCE, High pressure, low pressure, plasma
Kinetics(Deal Grove + deviations),
 SiO_2 structure, **Defects in Si**, Charges in SiO_2
Characterization of SiO_2 , electrical prop etc.

Oxide deposition

CVD, ALD, Sputtering

Anodic oxidation

FYS4310 Oxidation

mostly SiO_2 applications, formation, properties

- What is the oxide used for ?
- List of oxidation methods: 1 Thermal Oxide
- Deal Grove (DG) model
- Verification, deviation from DG model
- Properties of oxide, struct, el, opt, diffusion
- Defects during oxidation
- Electrical properties of Si/ SiO_2
- Other methods of oxide preparation, Alternatives

FYS4310 OXIDATION

What is SiO_2 used for?

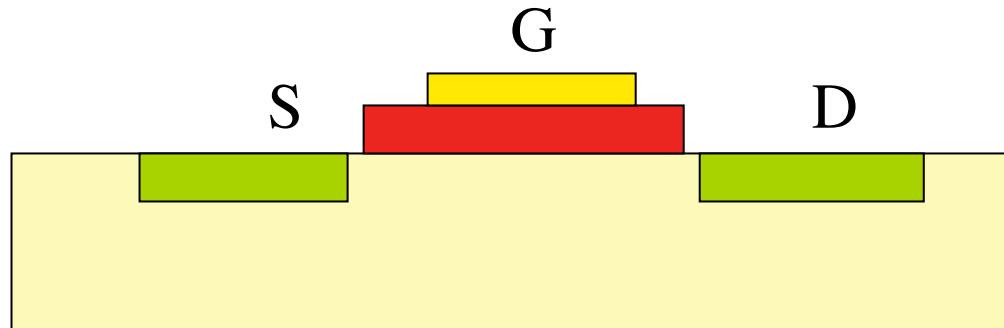
- Surface passivation
- Gate oxide
- Diffusion mask
- Insulation
- Film with low thermal conductivity
- FOX (passivation, insulation)

FYS4310 oxidation PASSIVATION

- The need for passivating surface:
Wants Si surface electrically neutral and
insensitive to atmosphere
- The major reason why Si is the dominating
semiconductor for electronic devices - is -
excellent passivation, and insulation, diffusion
mask, etching selectivity

FYS4310 oxidation

Gate Oxide

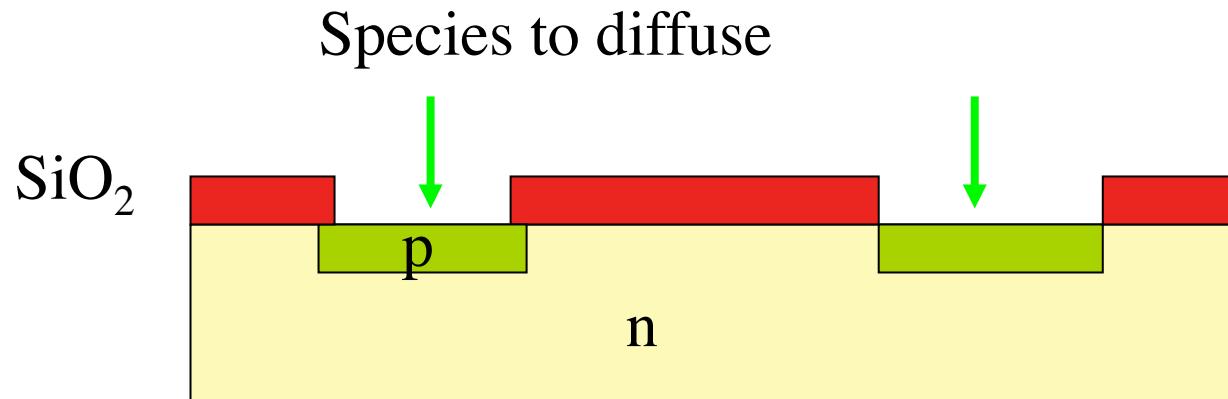


- Very high quality required
- High breakdown strength
- Extreme uniformity
- No electrical charges

Thermal SiO₂ deliver!

FYS4310 oxidation

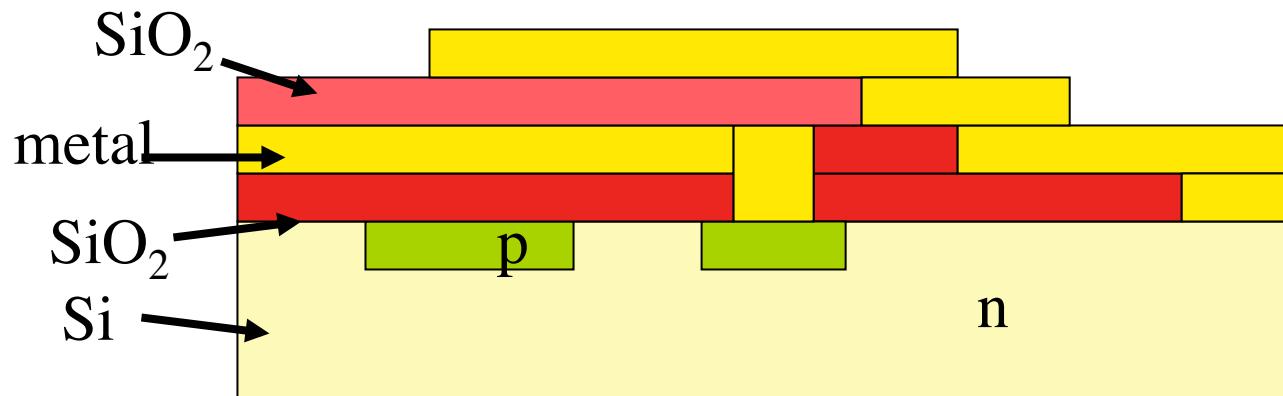
Diffusion/Implantation mask



- SiO_2 can be photo-lithographically patterned on Si
- Demands diffusivity in SiO_2 low compared to Si
- Ions stops in SiO_2

FYS34310 oxidation

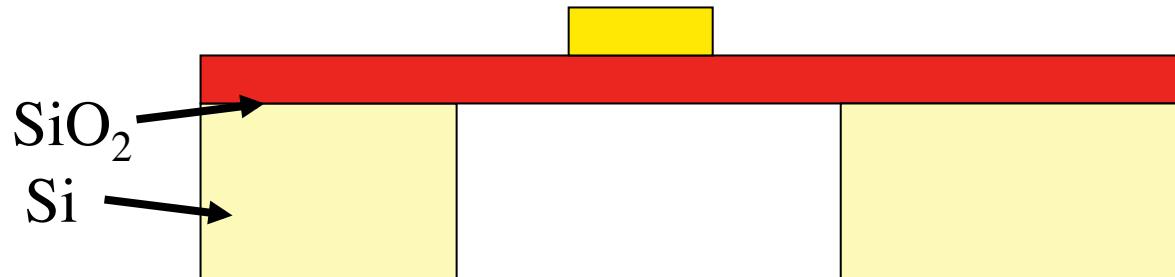
Insulation



- SiO₂ film should be pinhole free
- Low breakdown,
- Low leakage
- Thermal or deposited

FYS4310 oxidation

Film with low thermal conductivity



- For sensor applications
- Si₃N₄ more common,
- Thick porous SiO₂ maybe?

List of oxidation methods

- **Thermal oxidation**
- Low pressure oxidation,
- High pressure oxidation
- Plasma oxidation
- RTO, Rapid Thermal Oxidation
- Anodic Oxidation
- Oxide deposition, CVD, sputter, etc.

Oxidation Deal Grove model

- Important because it is simple.
 - It gives many predictions
 - These are testable
 - Simplifying assumptions
 - Testing justifies
 - Deviations from predictions defines part of parameter space
 - Deals with THERMAL DIFFUSION

Oxidation Deal Grove model

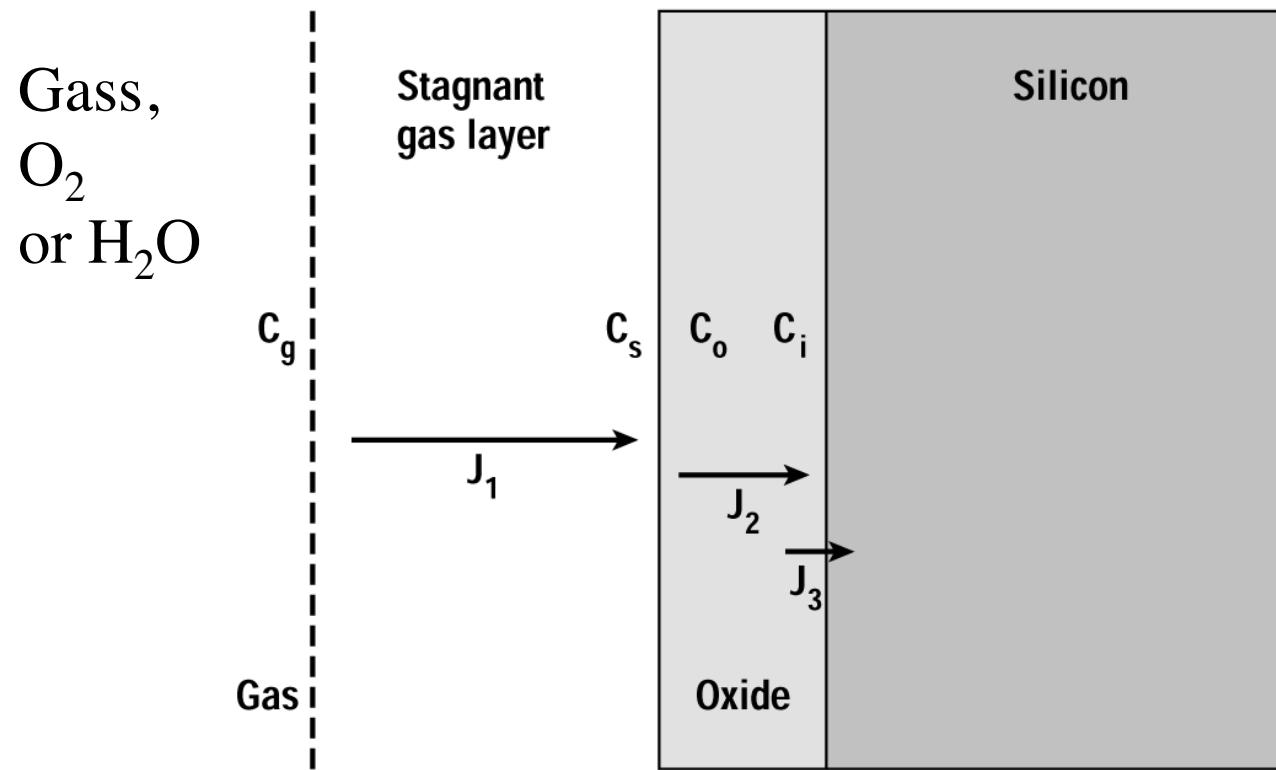


Figure 4.1 Schematic diagram of the oxidant flows during oxidation.

Deal Grove model, assumptions

Gas molecules, O₂ or H₂O
Diffuse in SiO₂
Growth at Si/SiO₂ interface
Henry's law valid
(No reaction in oxide,
molecular diffusion)
Stationary flow condition
Ficks 1st law valid

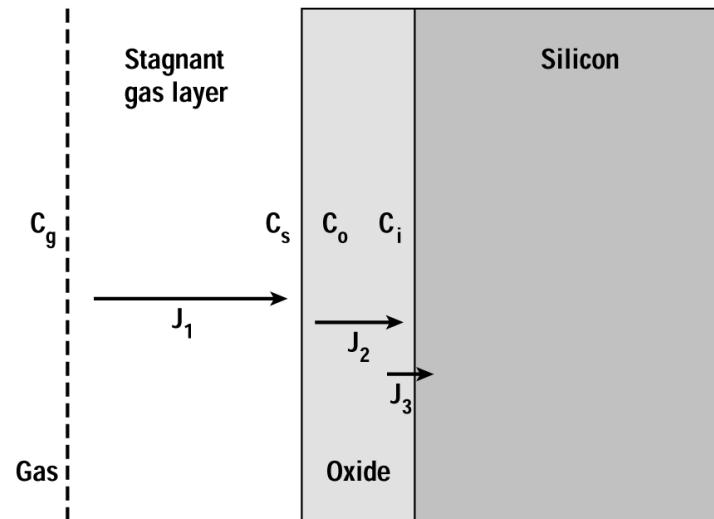


Figure 4.1 Schematic diagram of the oxidant flows during oxidation.

Deal Grove model, calculations

Want to calculate thickness, $x = x(t, \dots)$

J_1 , gas flux, given by Ficks law

$$J_1 = -D \frac{\partial C}{\partial x} = h_g (C_g - C_s)$$

J_2 , flux in oxide

$$J_2 = -D \frac{\partial C}{\partial x} = D \frac{C_0 - C_i}{x}$$

J_3 , flux on Si/SiO₂ interface

$$J_3 = k C_i$$

Need C_i expressed by observable parameters i.e., p_g

Need relationship between C_g and p_g , C_s and p_s , C_s and C_0

$$\text{Ideal gas } p_g = C_g kT \quad p_s = C_s kT$$

$$\text{Henry's law } C_0 = H p_s = H k T C_s$$

In steady flow $J_1 = J_2 = J_3$

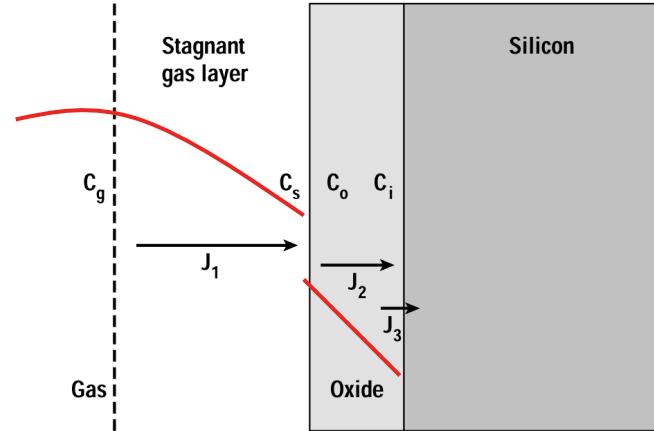


Figure 4.1 Schematic diagram of the oxidant flows during oxidation.

$$C_i = \frac{H p_g}{1 + \frac{k}{h} + \frac{kx}{D}} \quad \text{where } h = \frac{h_g}{H k T}$$

Deal Grove model, growth rate

Want to calculate $x = x(t, \dots)$

J_3 , flux on Si/SiO₂ interface

$$J_3 = kC_i \quad Ci = \frac{Hp_g}{1 + \frac{k}{h} + \frac{kx}{D}}$$

$$\frac{\partial x}{\partial t} = \frac{kCi}{N_1} = \frac{kHp_g}{N_1 \left(1 + \frac{k}{h} + \frac{kx(t)}{D}\right)}$$

Solution

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

where $A = 2D \left(\frac{1}{k} + \frac{1}{h} \right) \quad B = \frac{2DHp_g}{N_1} \quad \tau = \frac{x_0^2 + Ax_0}{B}$

Deal Grove model, Universal curve

Have calculated $x = x(t,..)$

$$B = \frac{2DHp_g}{N_1}$$

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

$$A = 2D\left(\frac{1}{k} + \frac{1}{h}\right)$$

$$\tau = \frac{x_0^2 + Ax_0}{B}$$

$$\frac{x}{A/2} = \sqrt{1 + \frac{t + \tau}{A^2/4B}} - 1$$

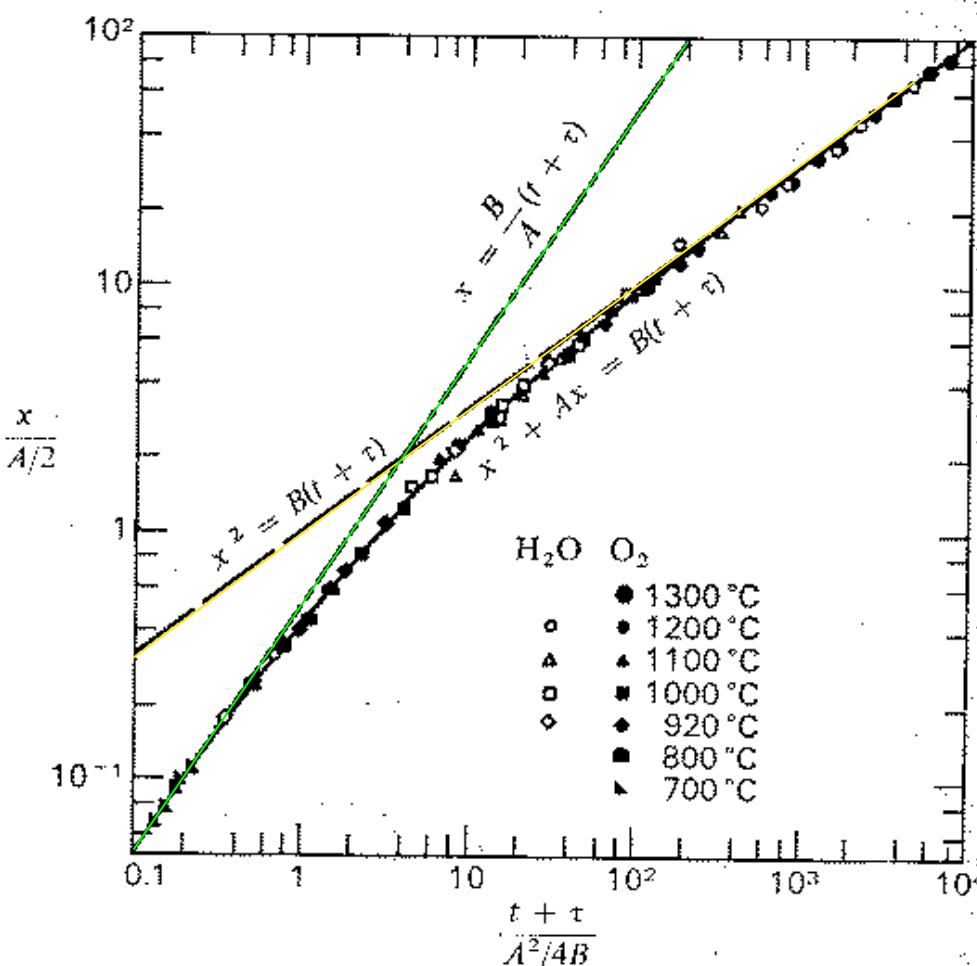
Thin oxide:

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

Thick oxide:

$$\underline{\underline{x^2 \approx B(t + \tau)}}$$

Linear rate constant B/A
Parabolic rate constant B



Arrhenius B

Have calculated $x = x(t,..)$

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

$$A = 2D\left(\frac{1}{k} + \frac{1}{h}\right)$$

$$B = \frac{2DHp_g}{N_1}$$

$$\tau = \frac{x_0^2 + Ax_0}{B}$$

Experimental values

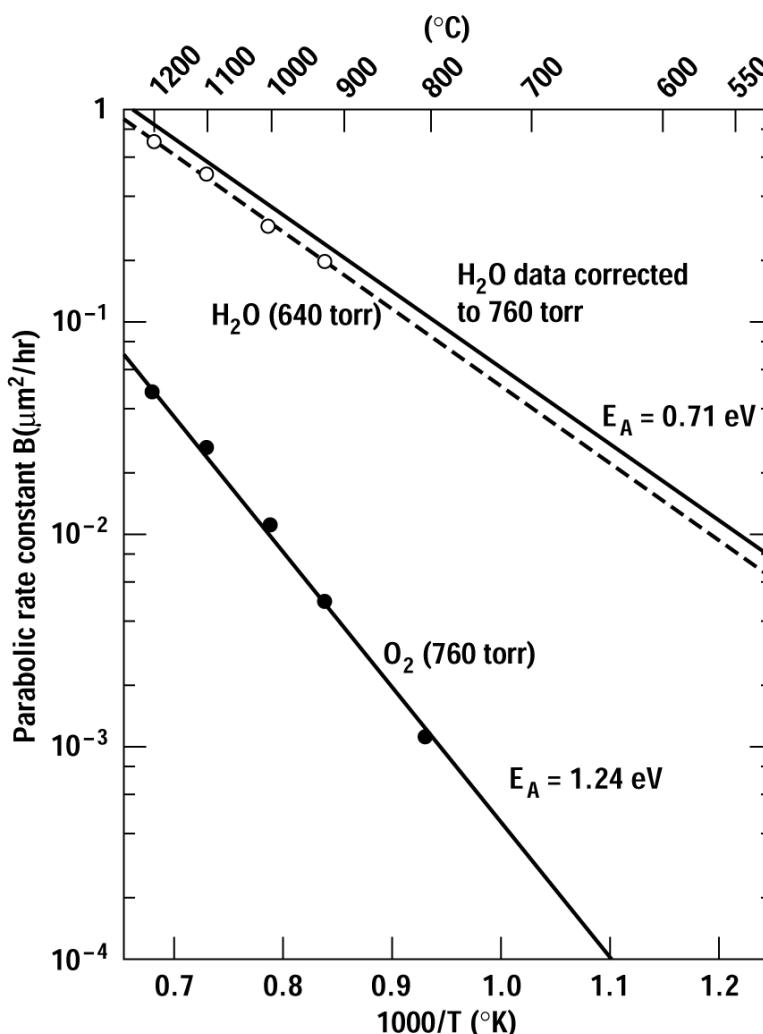


Figure 4.2 Arrhenius plot of the B oxidation coefficient. The wet parameters depend on the H_2O concentration and therefore on the gas flows and pyrolysis conditions (after Deal and Grove).

Aarhenius B/A

Have calculated $x = x(t,..)$

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

$$A = 2D\left(\frac{1}{k} + \frac{1}{h}\right)$$

$$B = \frac{2DHp_g}{N_1}$$

$$\frac{B}{A} = \frac{Hp_g}{N_1\left(\frac{1}{k} + \frac{1}{h}\right)}$$

$$\tau = \frac{x_0^2 + Ax_0}{B}$$

Experimental values

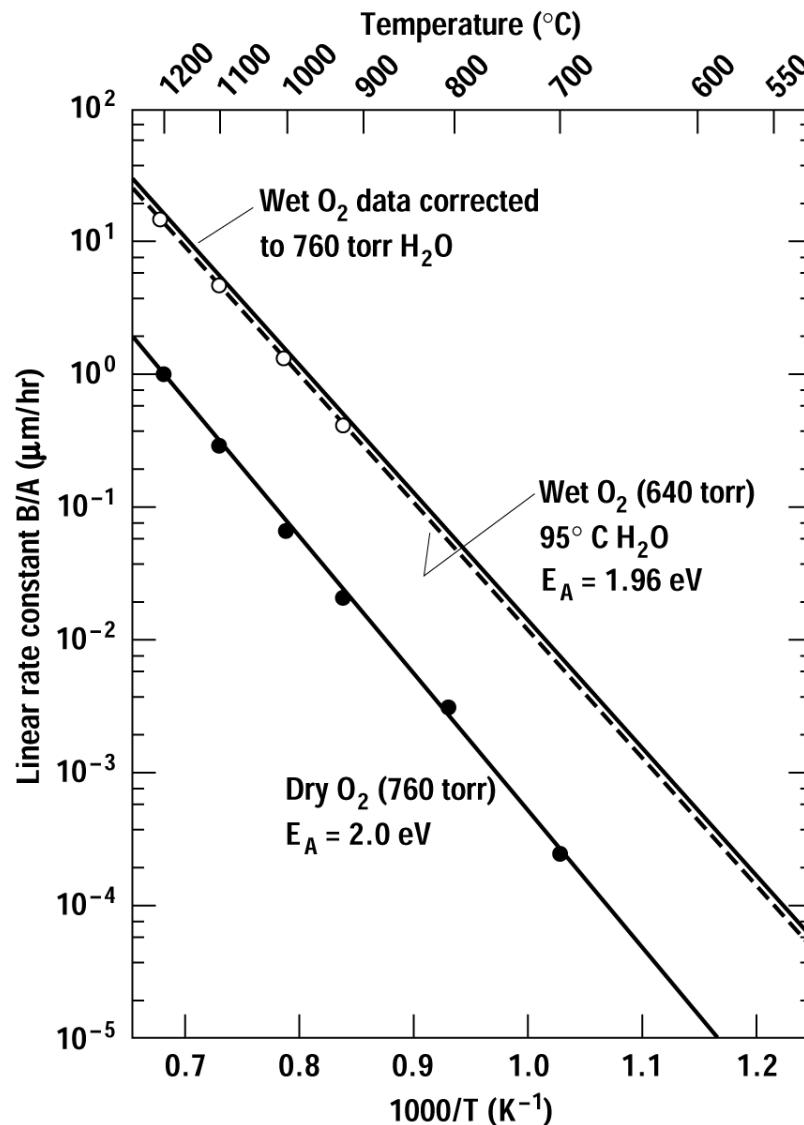


Figure 4.3 Arrhenius plot of the ratio (B/A) of the oxidation parameters (after Deal and Grove).

Pressure dependence

Experimental values

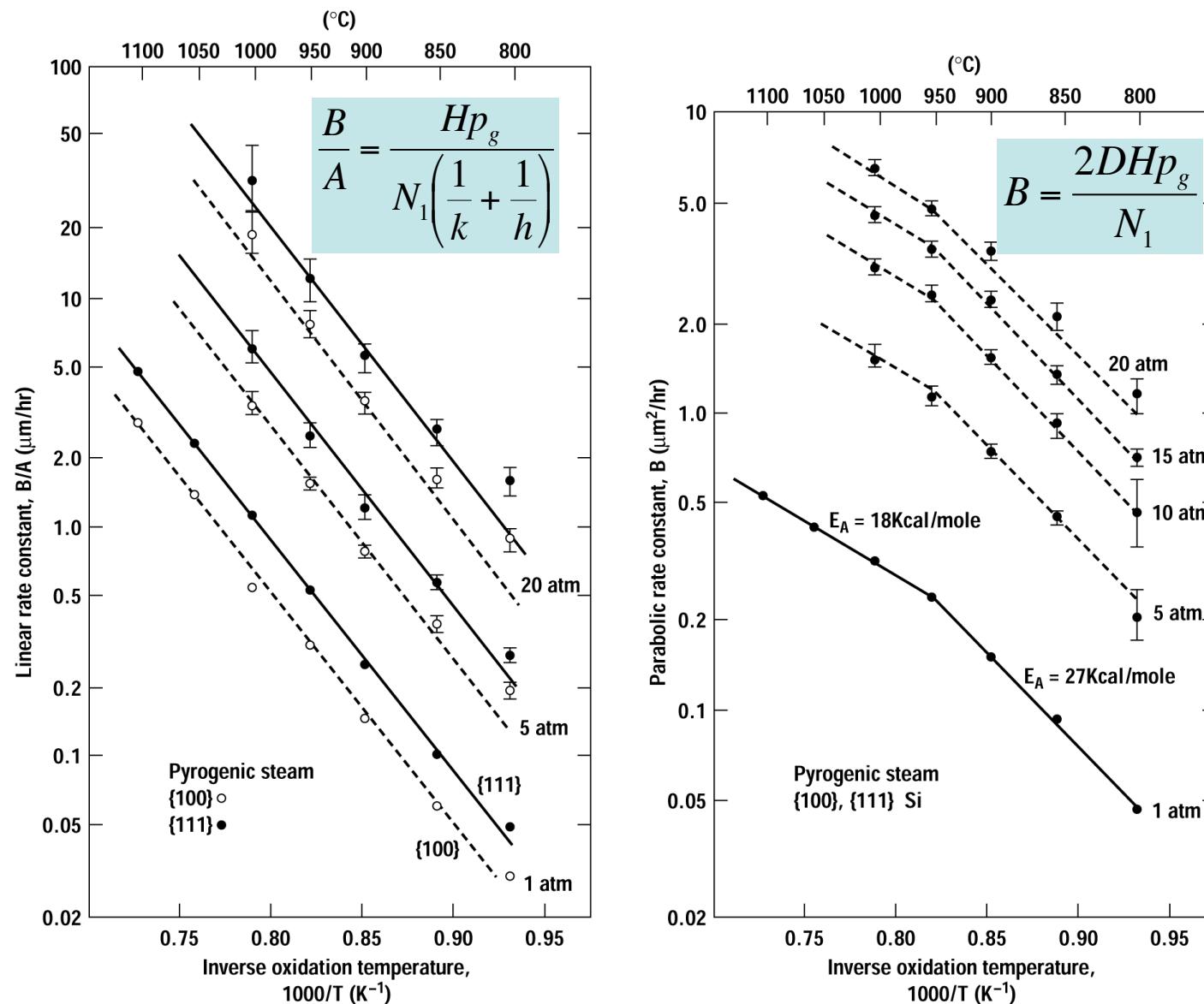


Figure 4.5 High pressure studies of the parabolic and linear rate coefficients in steam (after Razouk *et al.*, reprinted by permission, *The Electrochemical Society*).

H₂O versus O₂ oxidation (wet vs dry)

$$B_{H_2O} > B_{O_2}$$

$$D_{H_2O} < D_{O_2}$$

$$C^*_{H_2O} \gg C^*_{O_2}$$

(some textbook authors disagree)

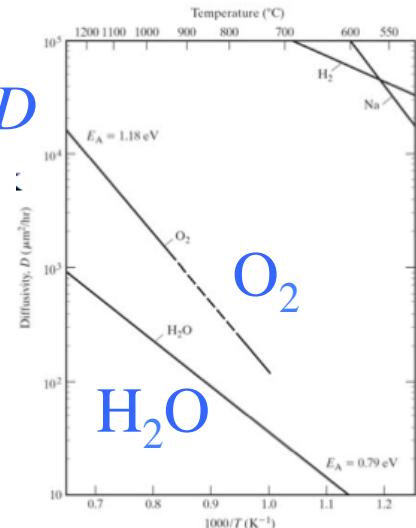
$$(B/A)_{H_2O} > (B/A)_{O_2}$$

$$B = \frac{2DHp_g}{N_1} = \frac{2DC^*}{N_1}$$

C*: equilibrium conc

This is one set of data

$$\frac{B}{A} = \frac{Hp_g}{N_1 \left(\frac{1}{k} + \frac{1}{h} \right)} = \frac{C^*}{N_1 \left(\frac{1}{k} + \frac{1}{h} \right)}$$



B B/A for P doping

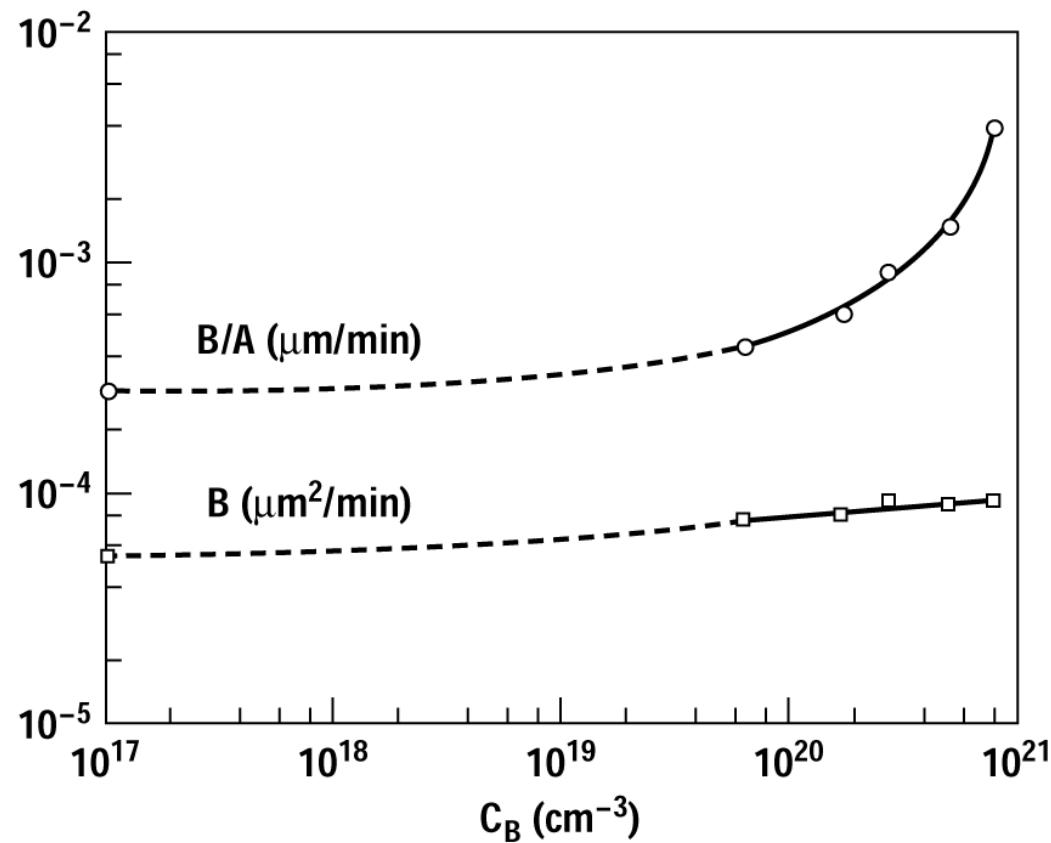


Figure 4.19 Oxidation rate coefficients for dry oxygen at 900°C as functions of the surface concentration of phosphorus (*after Ho et al., reprinted by permission, The Electrochemical Society*).

B dependence growth rate

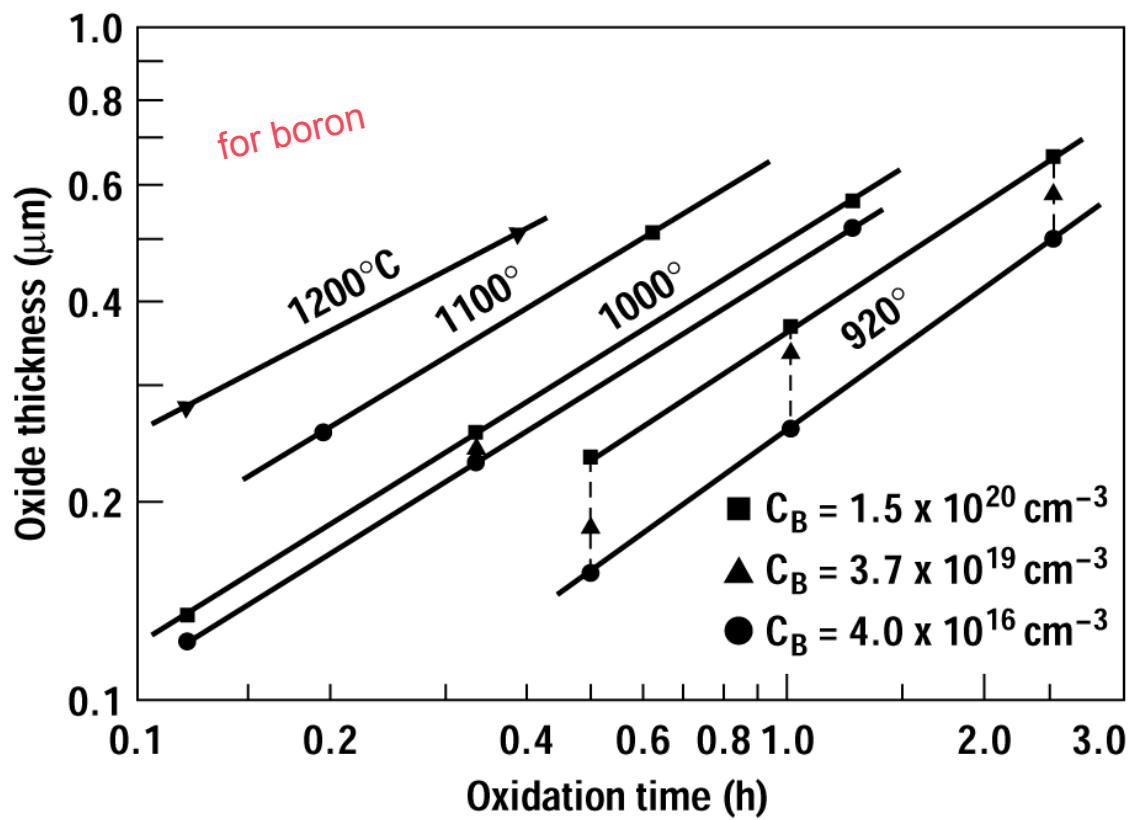
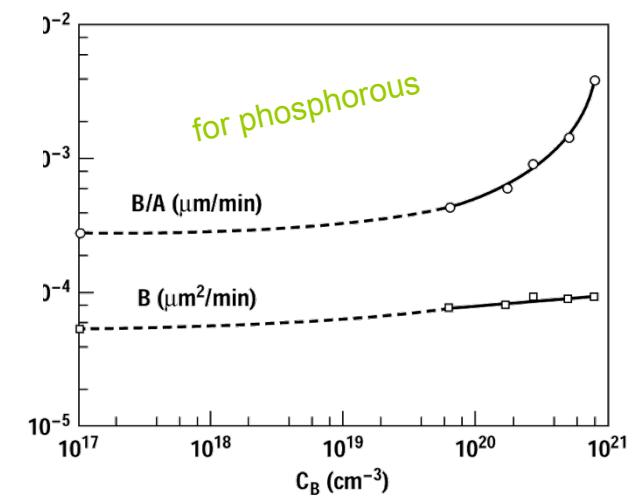


Figure 4.18 Silicon dioxide thickness versus wet oxidation time for three different surface concentrations of boron (after Deal *et al.*, reprinted by permission, *The Electrochemical Society*).



Segregation

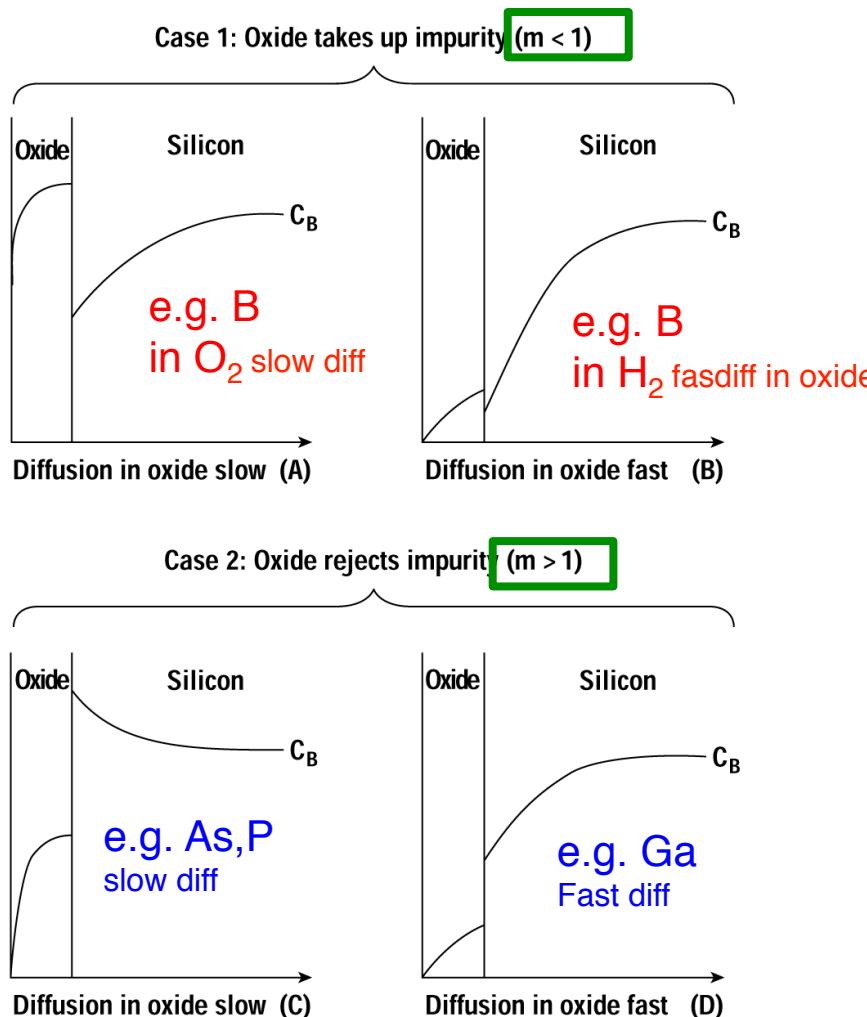


Figure 4.16 The effect of thermal oxidation on the impurity distribution in silicon and silicon dioxide.
 (A) Slow diffusion in oxide, $m < 1$ (boron in neutral or oxidizing ambient); (B) fast diffusion in oxide, $m < 1$ (boron in hydrogen ambient); (C) slow diffuser in oxide, $m > 1$ (phosphorus, arsenic); (D) fast diffuser in oxide, $m > 1$ (gallium) (*after Grove et al.*).

B segregation

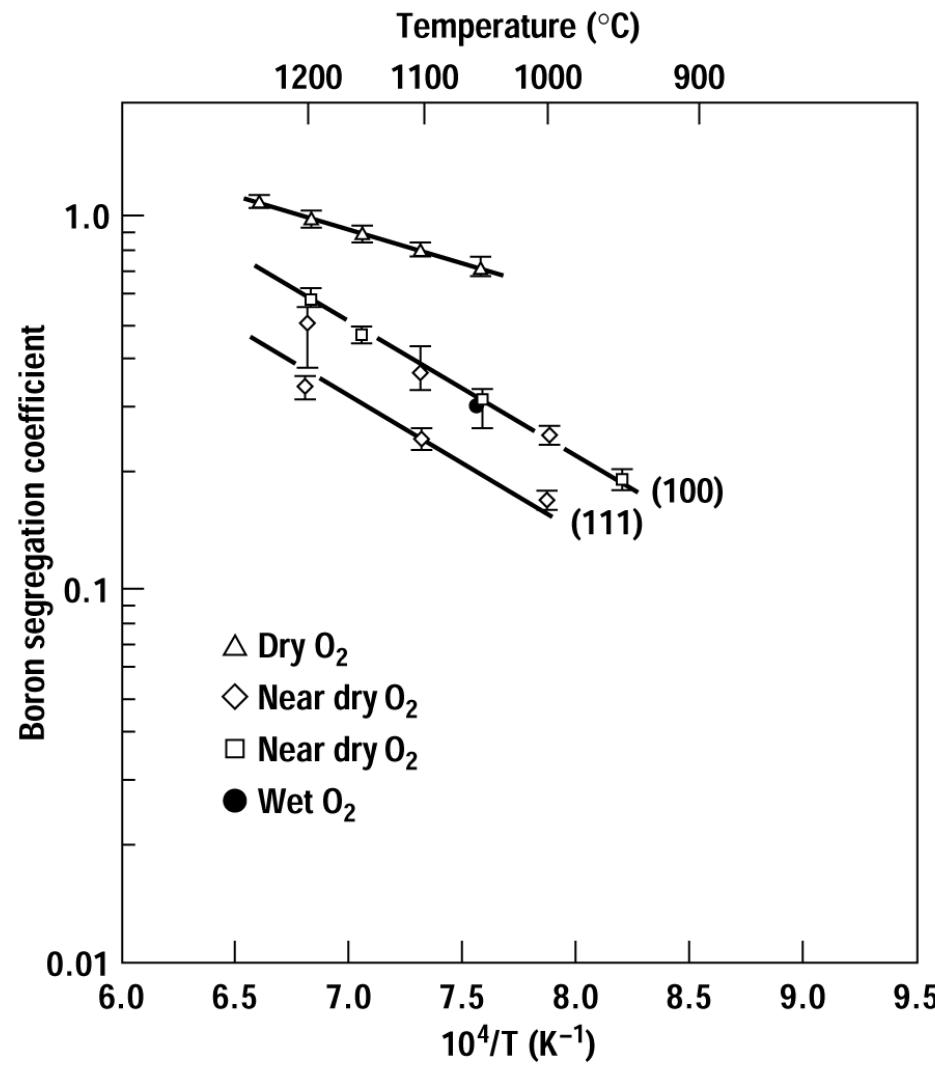


Figure 4.17 Temperature dependence of boron segregation coefficient for various types of oxidations (reprinted by permission, McGraw-Hill, after Katz).

Effect of Cl

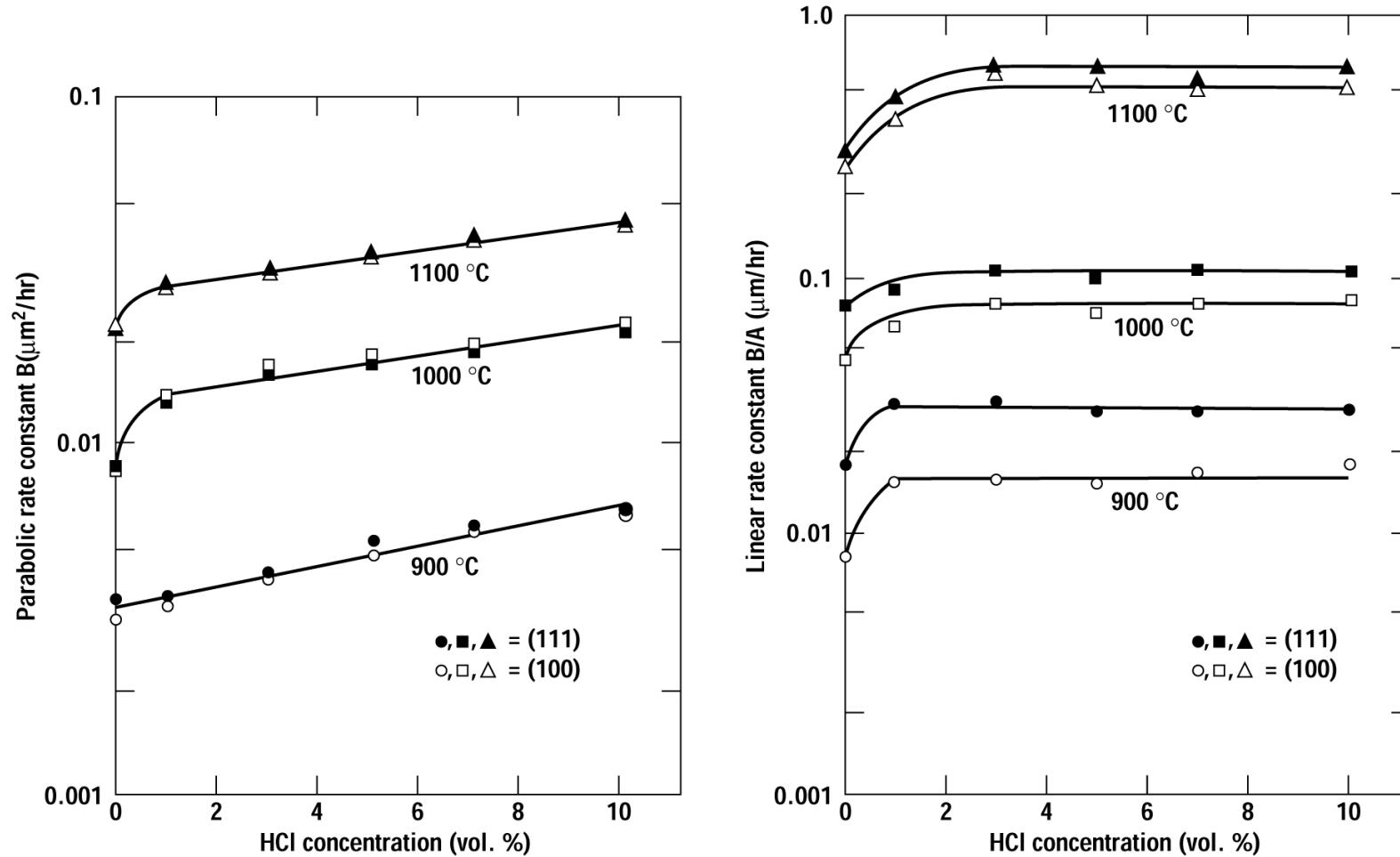


Figure 4.4 The effect of chlorine on the oxidation rate (after Hess and Deal, reprinted by permission, *The Electrochemical Society*).

Thin oxide

Deal Grove model not valid

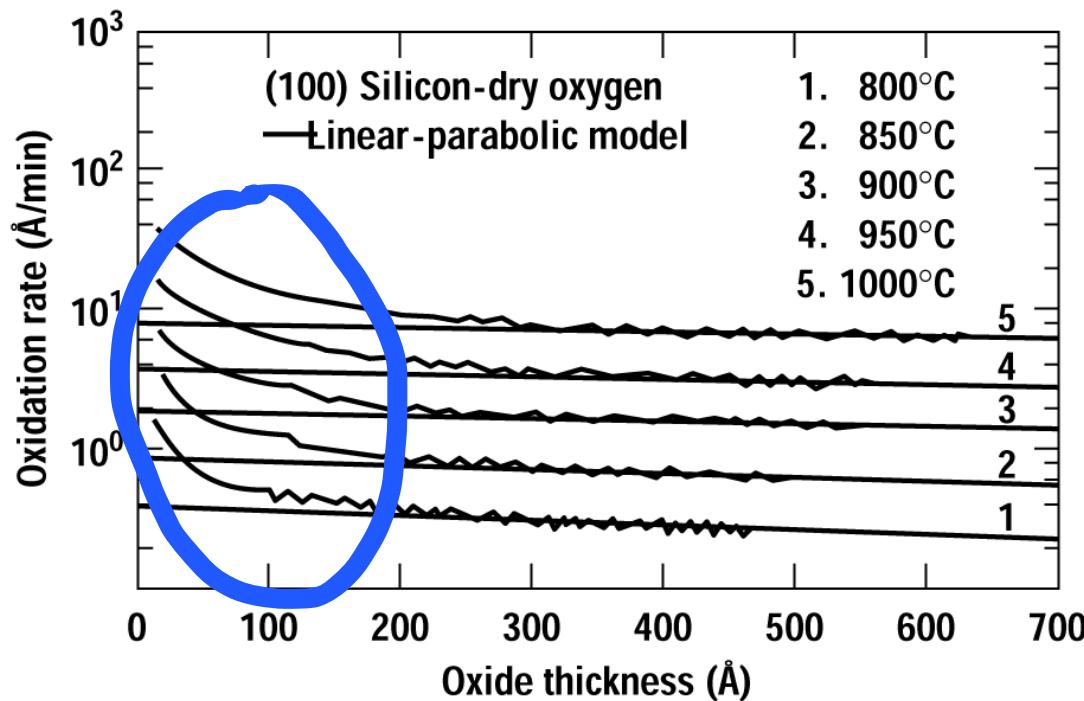


Figure 4.6 Oxide thickness dependence of the growth rate for very thin oxides oxidized in dry O_2 . The substrates are lightly doped (100) silicon (*from Massoud et al., reprinted by permission, The Electrochemical Society*).

This deviation from D.G. model is larger for O_2 than for H_2O

Very many models presented, No definite 'winners' IMHO

Oxidation induced stacking faults OSF

Why stacking faults? Self interstitials created , why?

Are OSF Good/bad , why? when? how?

Stacking fault length vs T

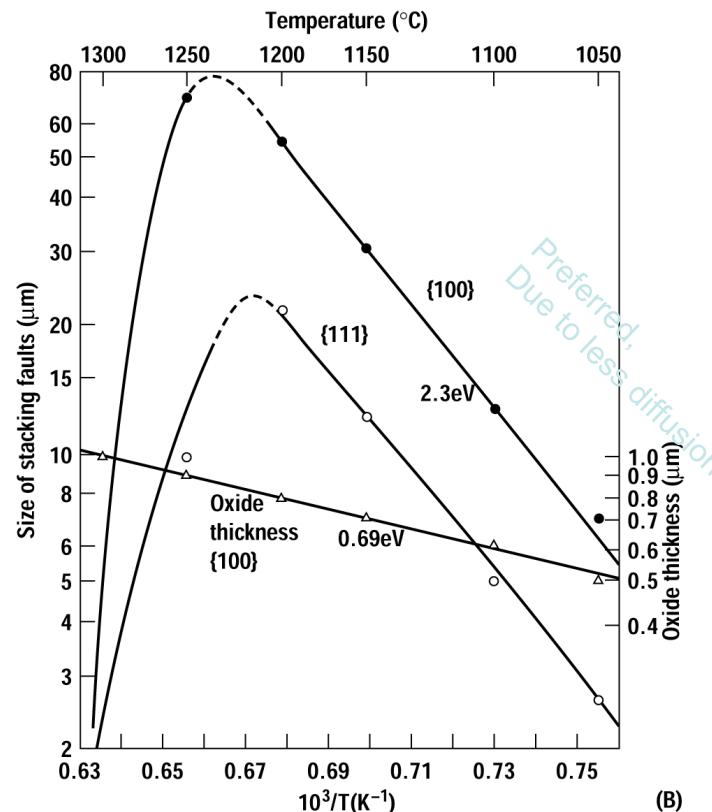
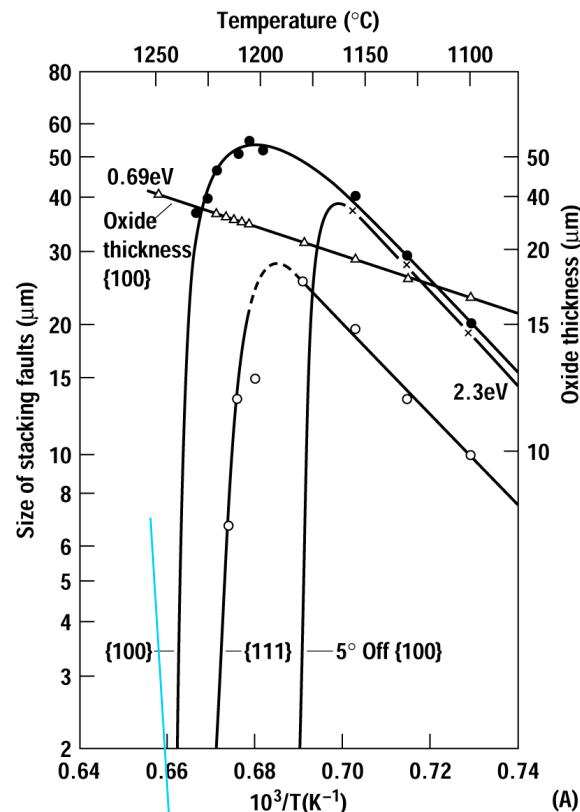


Figure 4.22 Typical stacking fault length as a function of temperature for (A) dry and (B) wet oxidation. Stacking faults are not favored at either high or low temperature (*after Hu*).

OSF grows initially, but then shrink

NB HCl ambient can prevent OSF

SiO_2 network

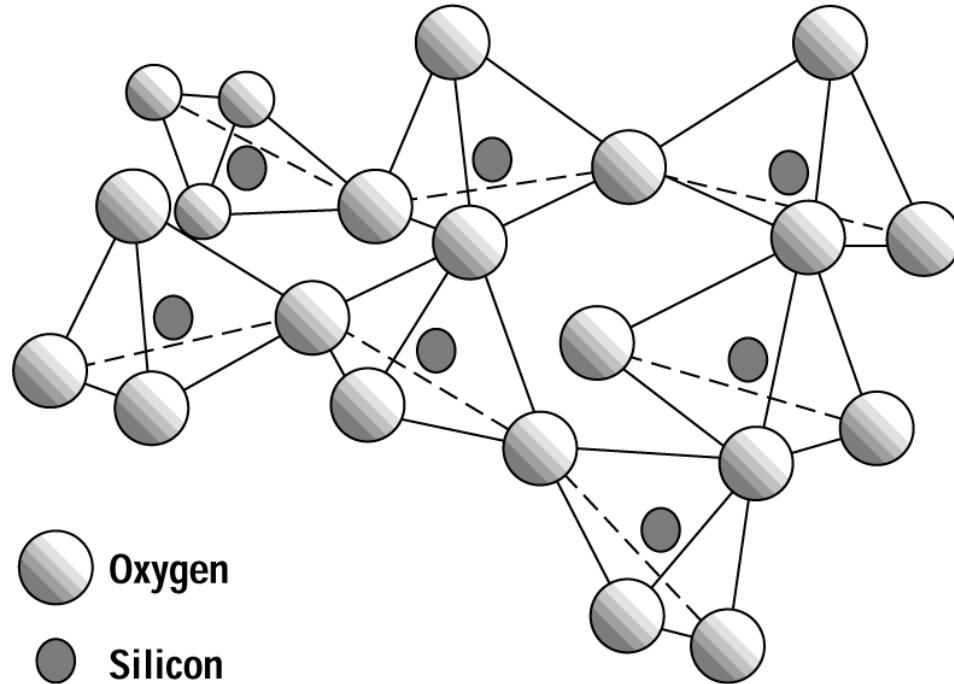
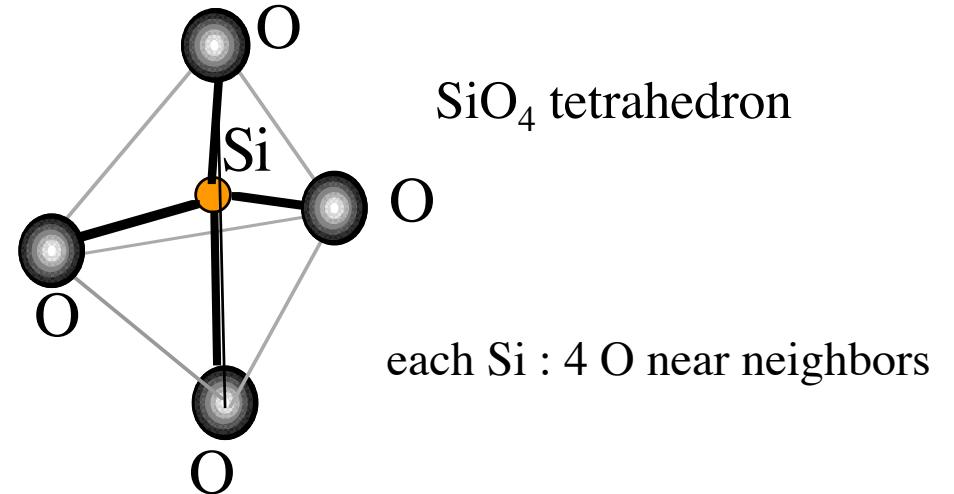


Figure 4.7 The physical structure of SiO_2 consists of silicon atoms sitting at the center of oxygen polyhedra.

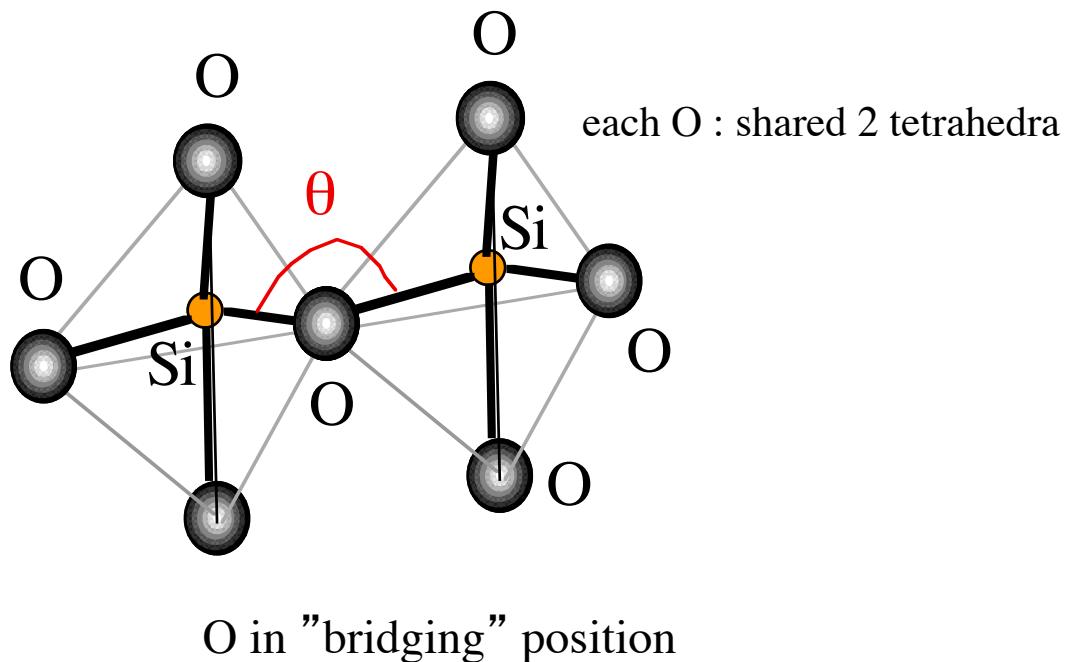
SiO_2 structure

Building block:



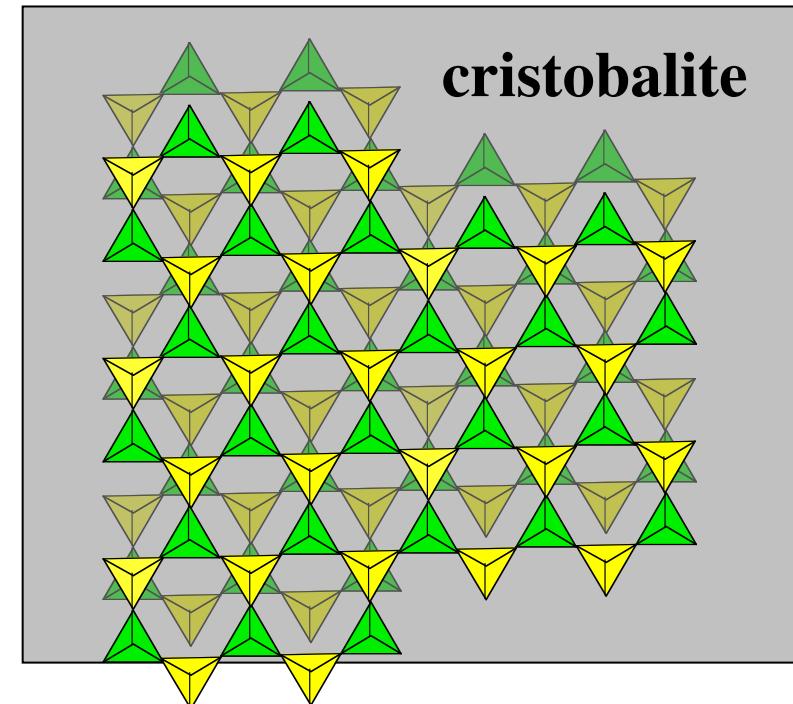
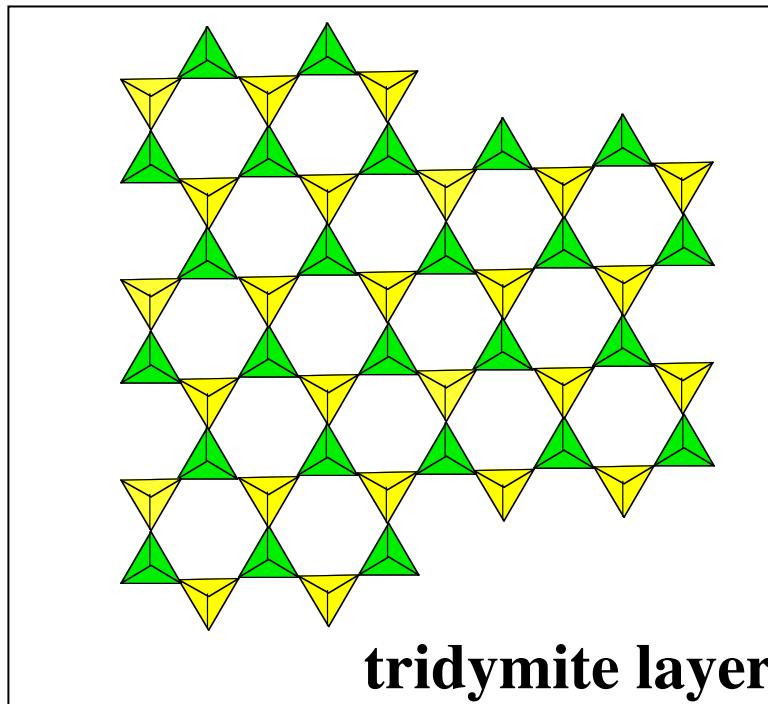
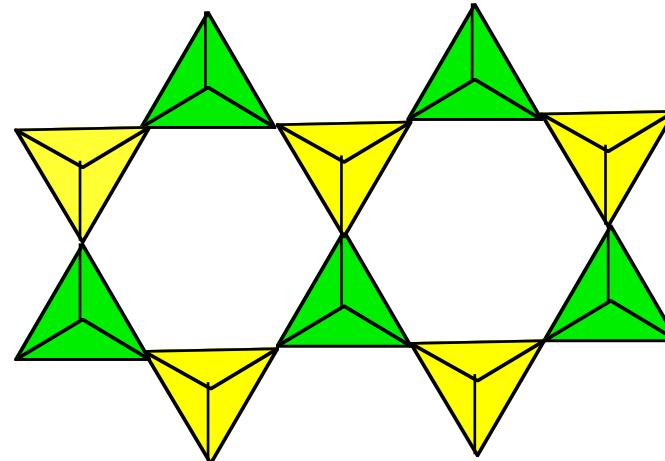
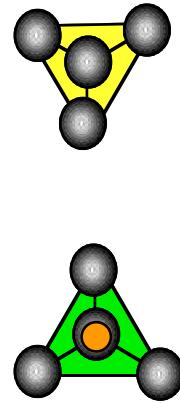
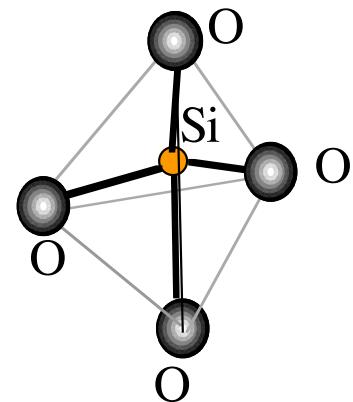
Network:

In various polymorphous
Xtal structures for SiO_2
The angle θ can vary much



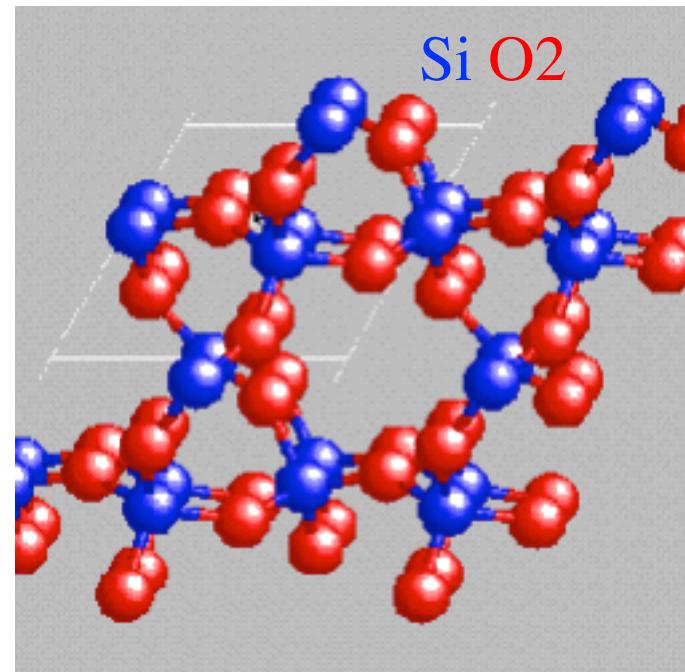
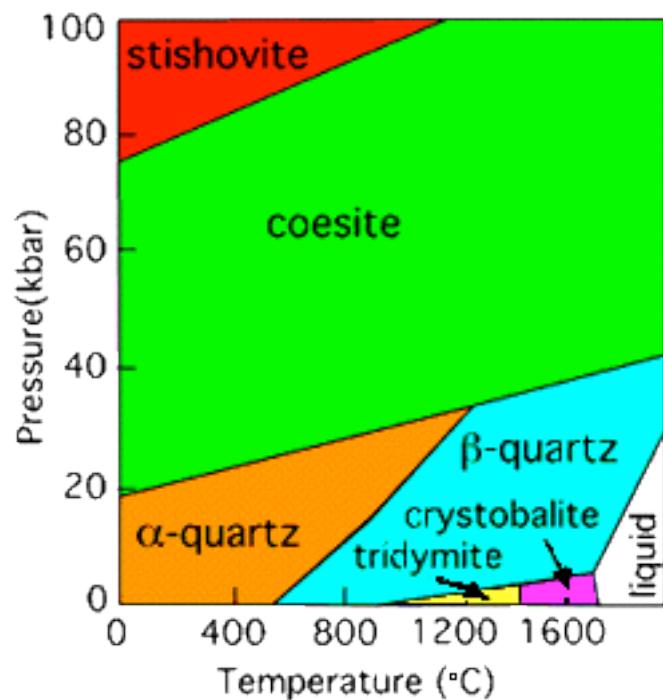
SiO_2 structure

SiO_4 tetrahedron



SiO_2 structure

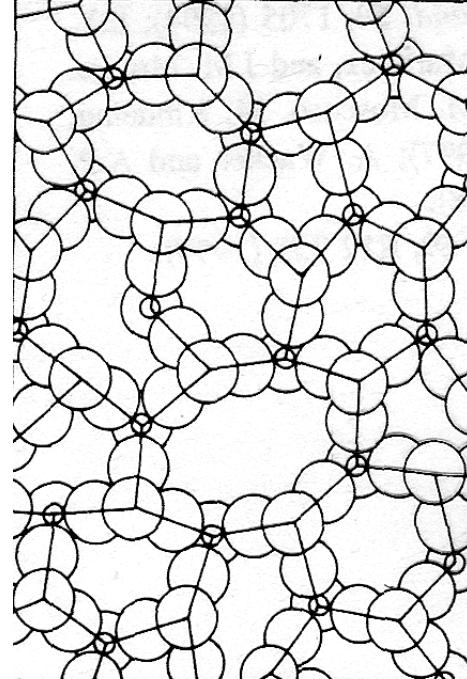
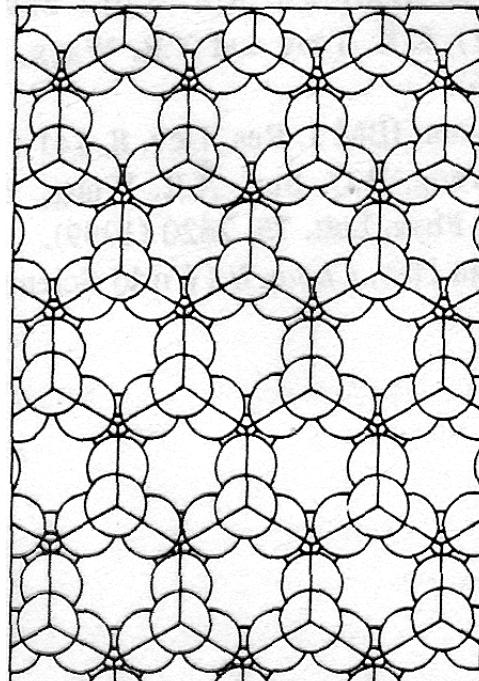
Different SiO_2 X-taline polymorphs



α -quarts

SiO_2 structure

Xtaline materials	Amorphous materials
Long range order	No long range order
Local order	Local order Atom distance, bonding angle
X-tal structure	Random network model



Oxide charges

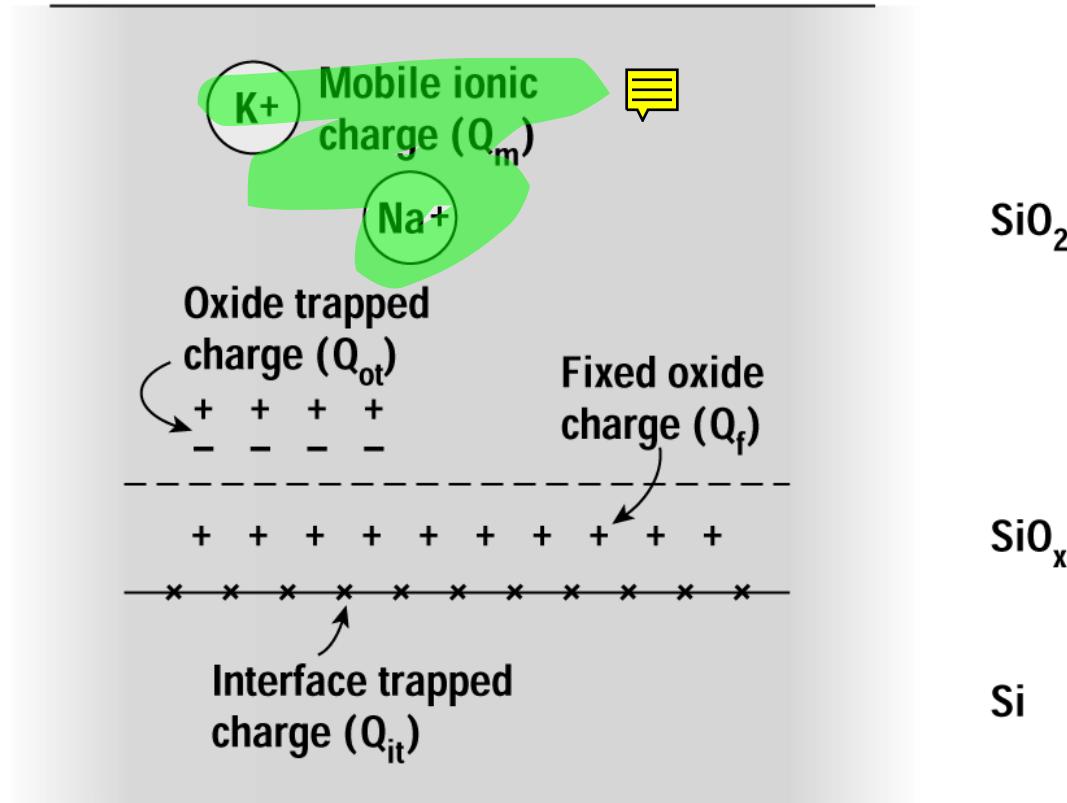
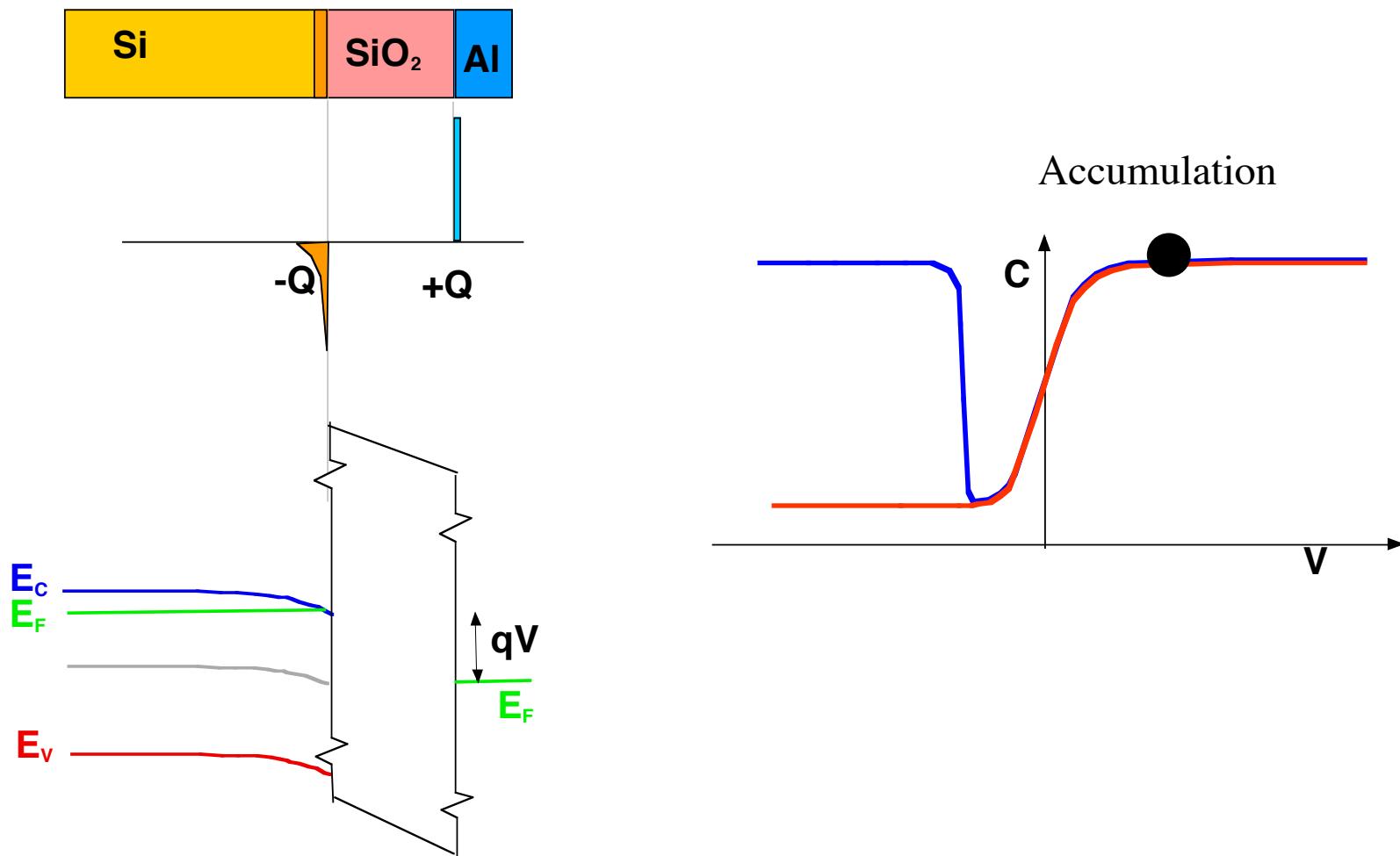


Figure 4.14 Silicon–silicon dioxide structure with mobile, fixed charge, and interface states (© 1980, IEEE, after Deal).

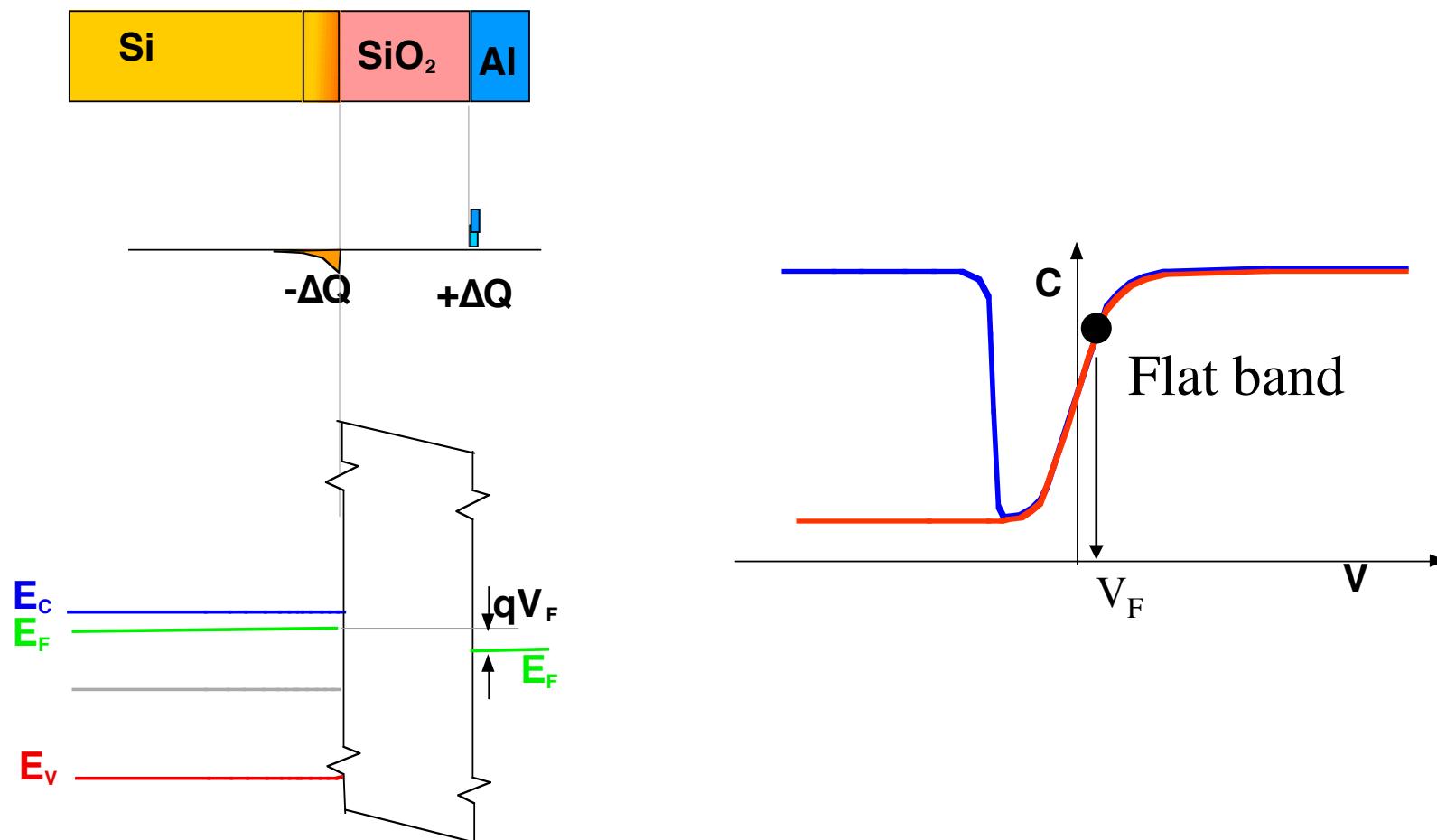
Oxide characterization CV

Accumulation



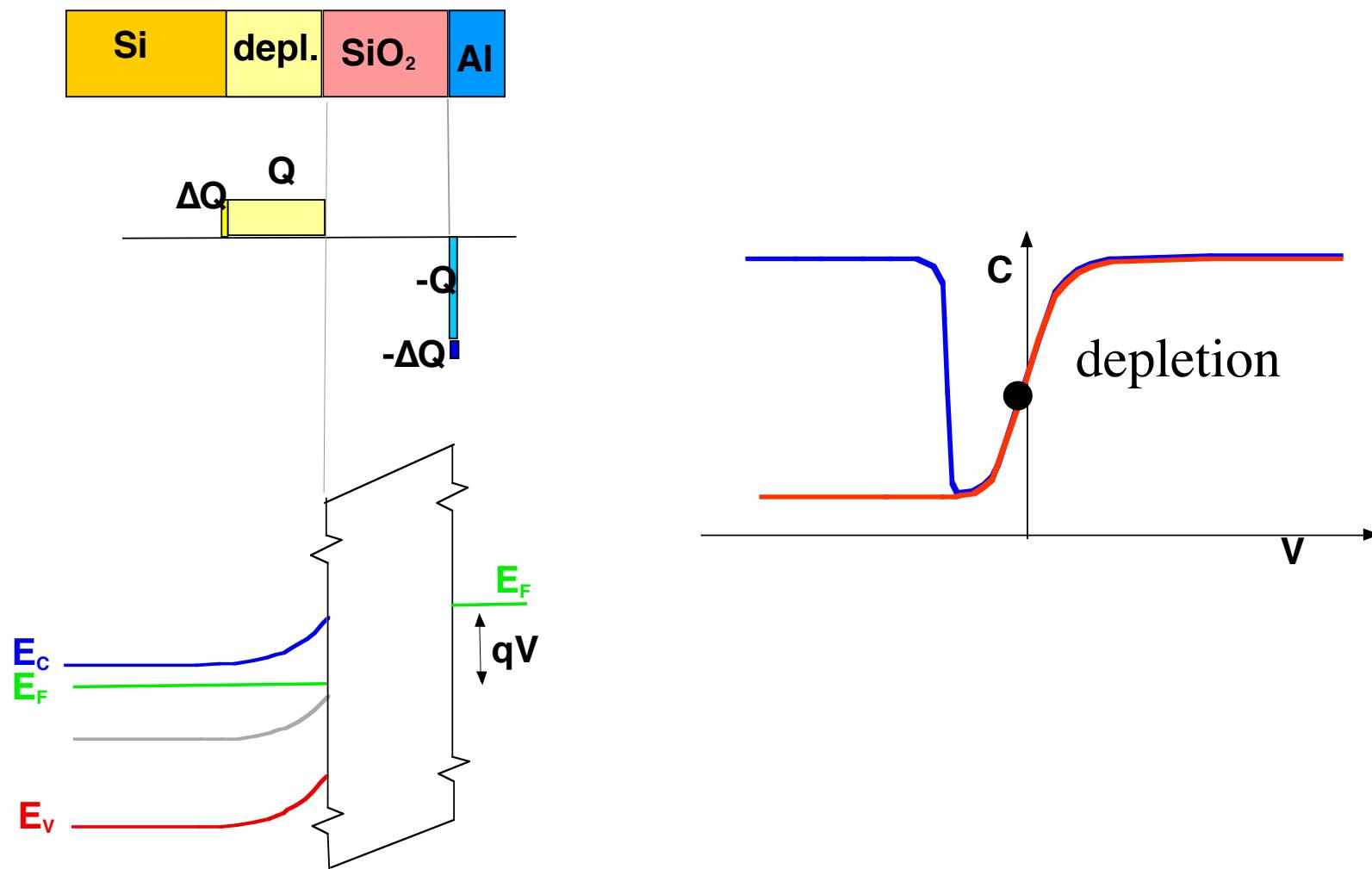
Oxide characterization CV

Flat band



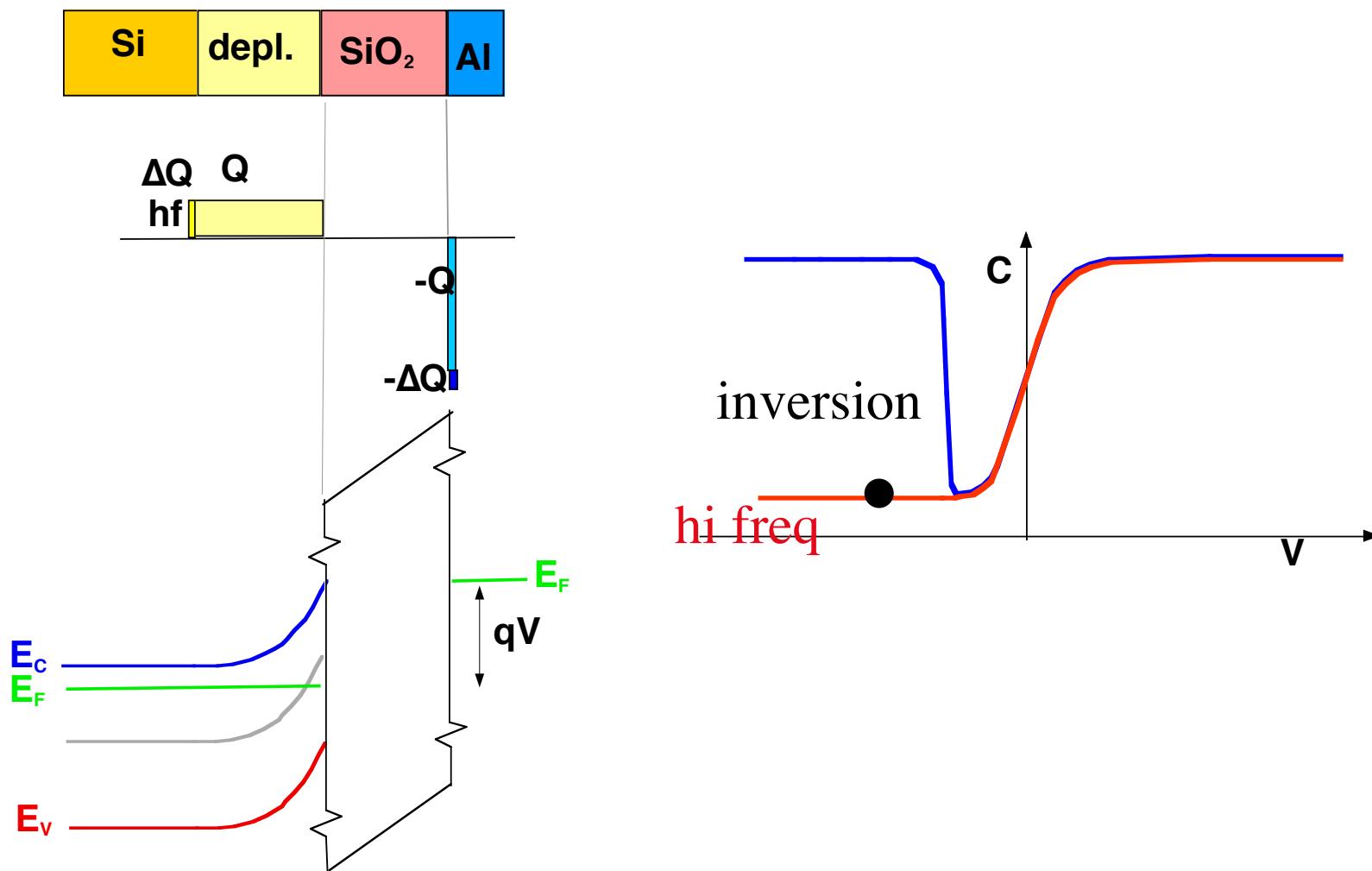
Oxide characterization CV

Depletion



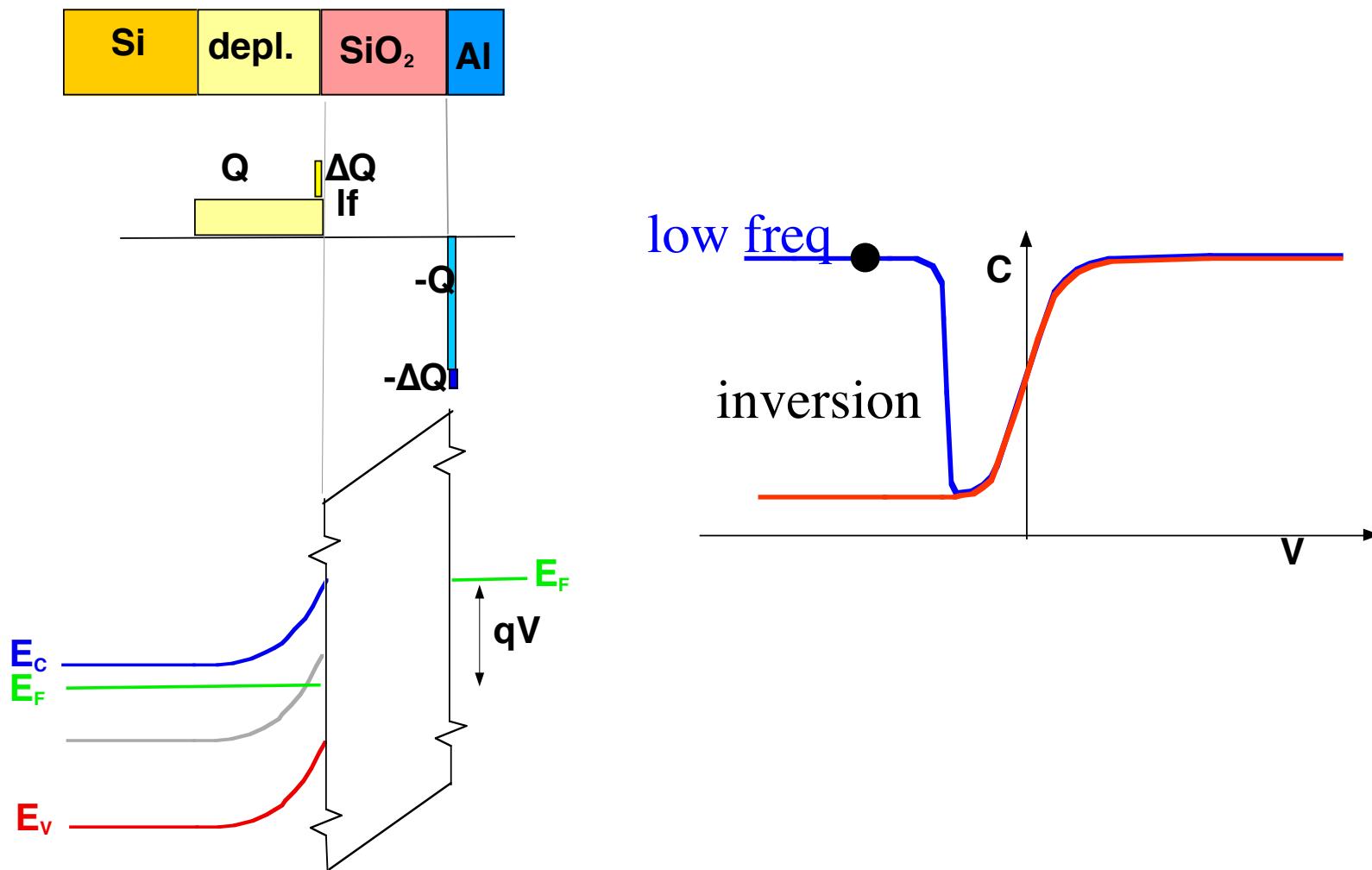
Oxide characterization CV

Inversion -high frequency



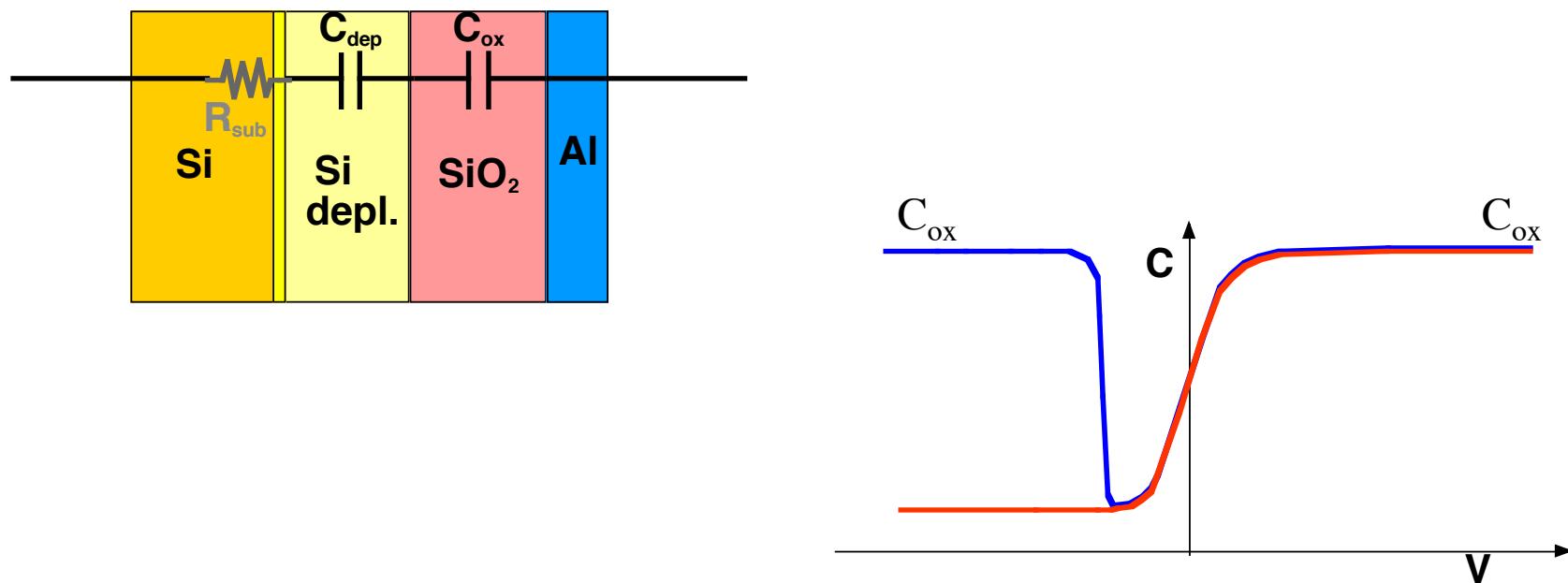
Oxide characterization CV

Inversion -low frequency



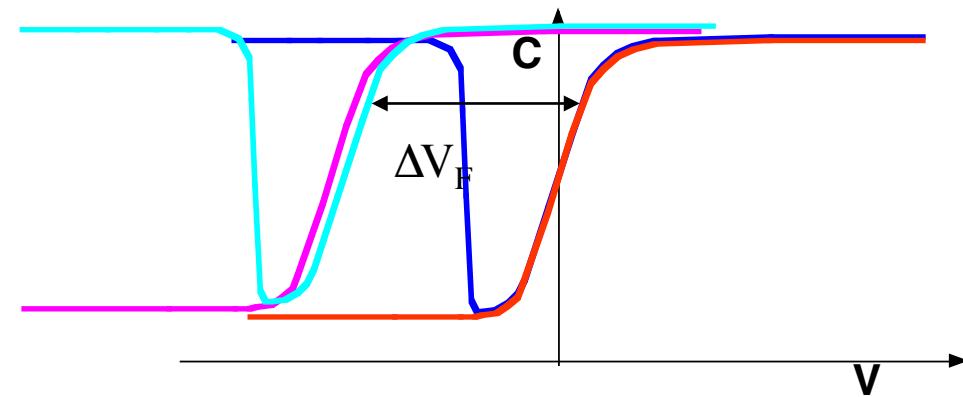
Oxide characterization CV

Electrical equivalent



Oxide characterization CV

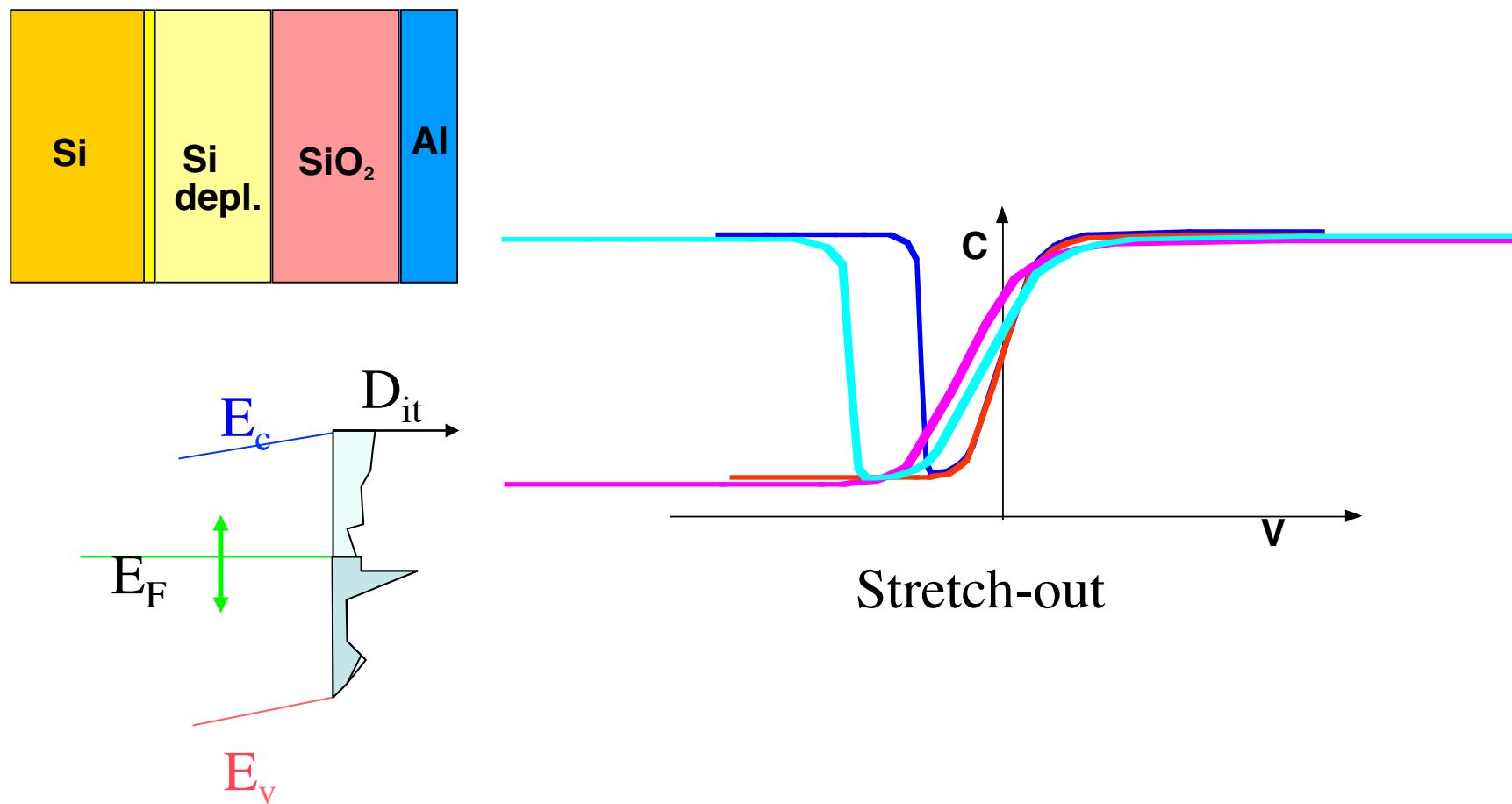
Effect of oxide charges



Change of flatband voltage

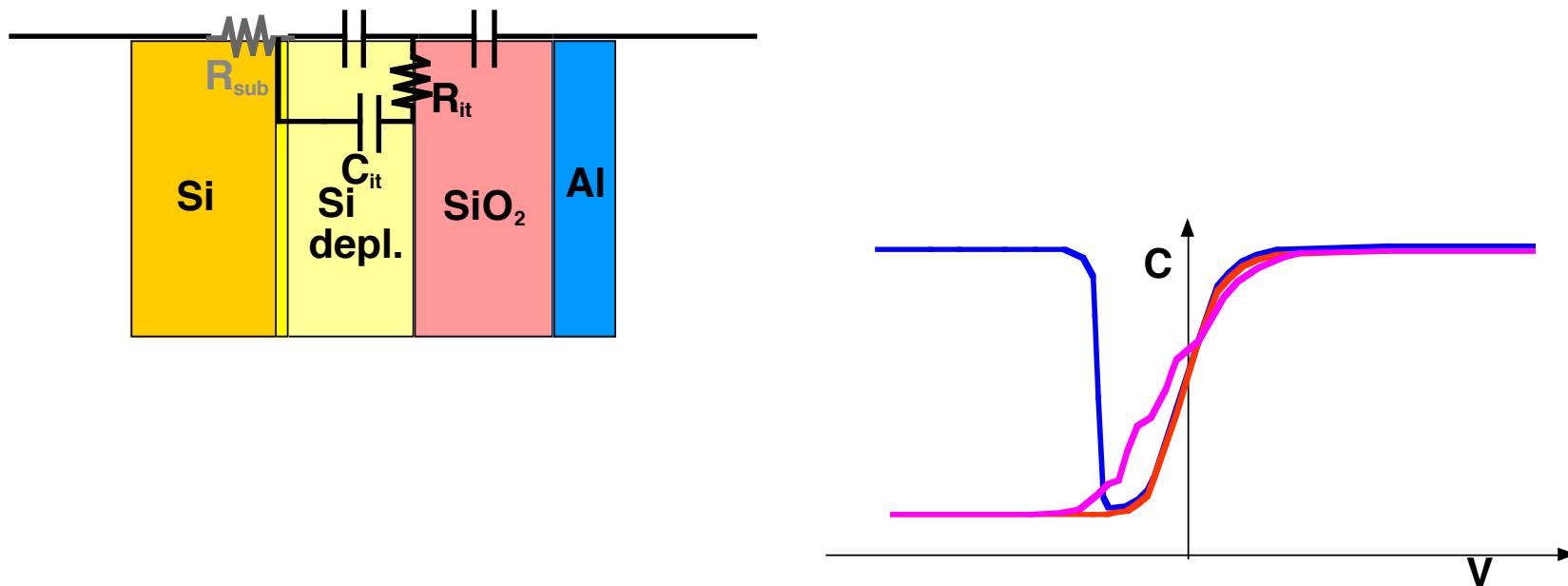
Oxide characterization CV

Effect of interface charges



Oxide characterization CV

Effect of interface charges



Stretch-out ++

If the frequency is high the interface states yields no extra capacitance when the state population can not follow the signal.

If the population responds to the signal, there is additional impedance, if it lags behind, it can be viewed as an RC term

CV hf D_{it} Q_{fix}

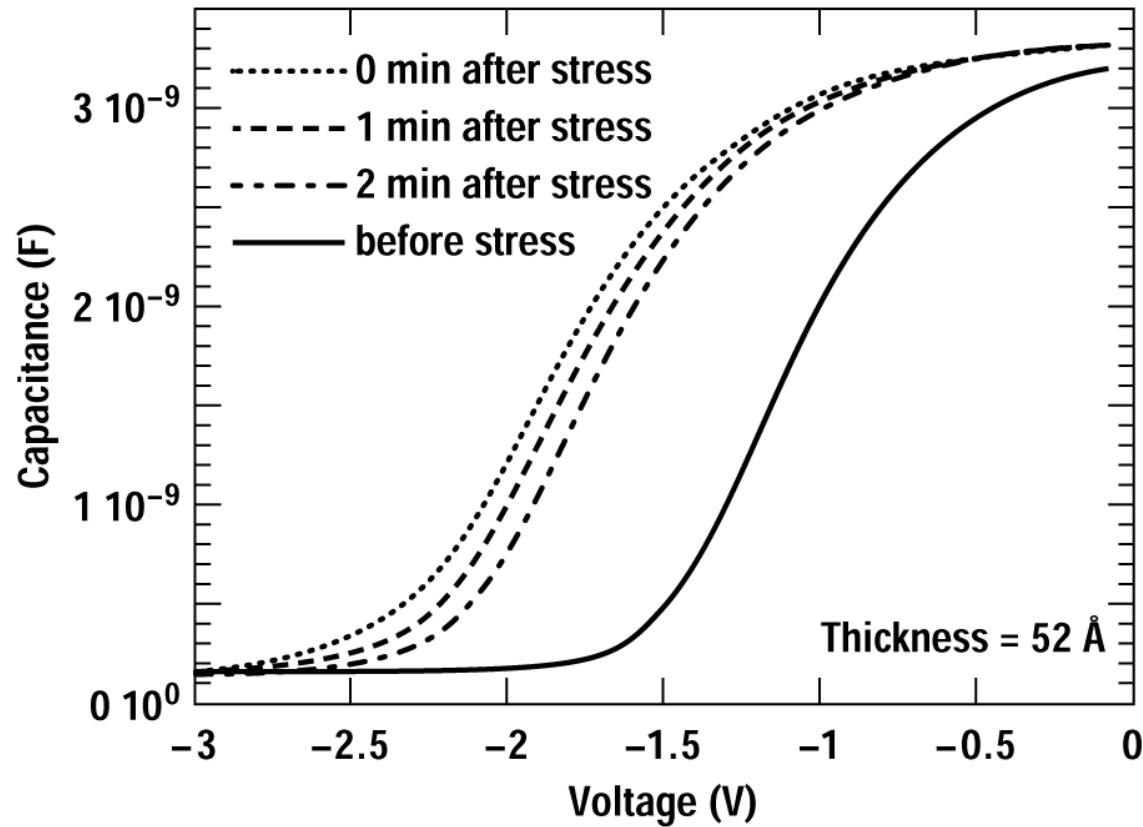


Figure 4.15 High frequency C–V traces showing the effects of interface states and fixed charge.

The Deal triangle

Surface states

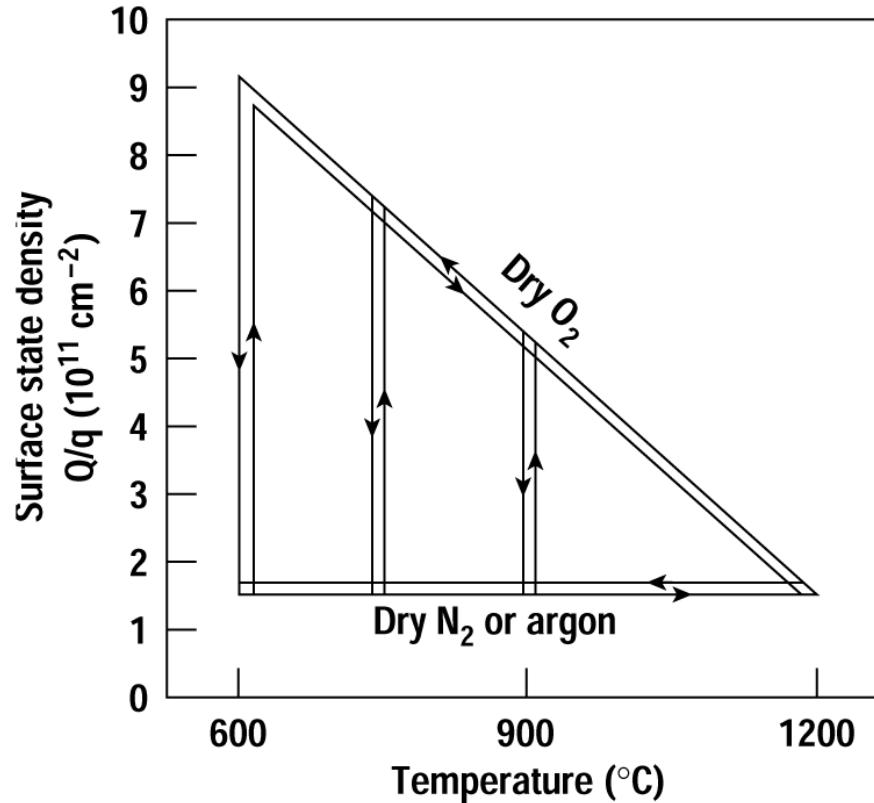


Figure 4.12 The Deal triangle showing the effects of a high-temperature inert (nitrogen or argon) postoxidation anneal on interface states and fixed charge density (*after Deal et al., reprinted by permission, The Electrochemical Society*).

CV temperature
bias stress

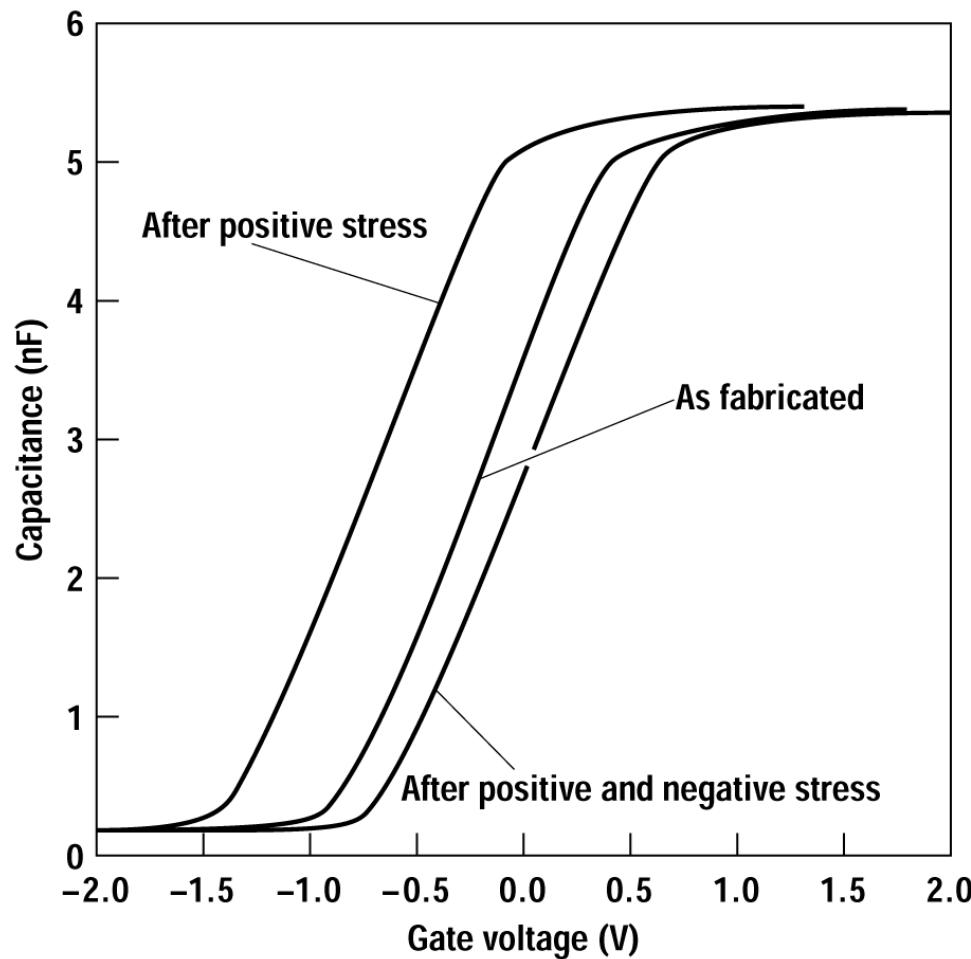


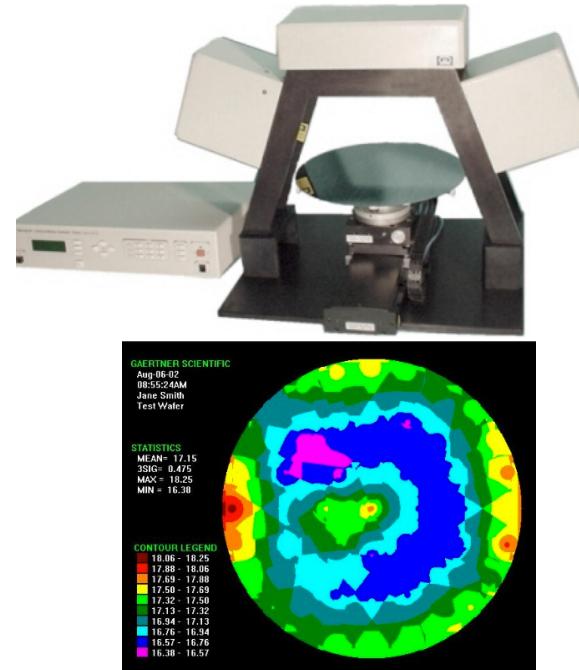
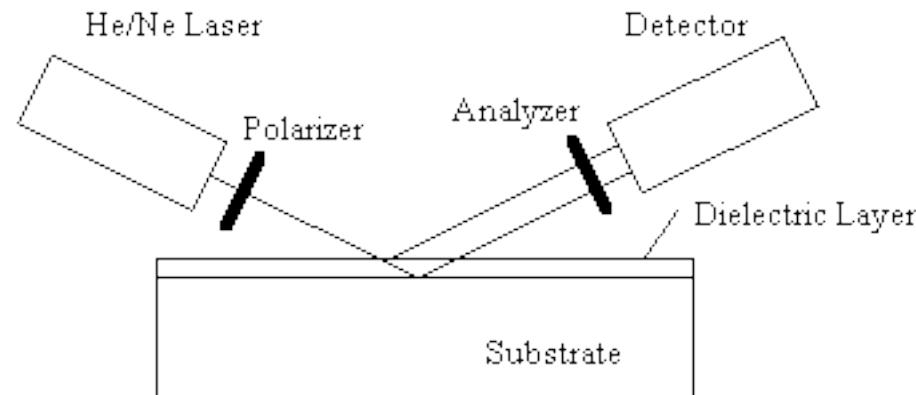
Figure 4.13 Typical C–V traces from temperature bias stress measurements of an oxide contaminated with a positive ion impurity.

Oxide characterization elipsometry

Measure the refractive index and the thickness.

The reflection at a dielectric interface depends on the polarization of the light

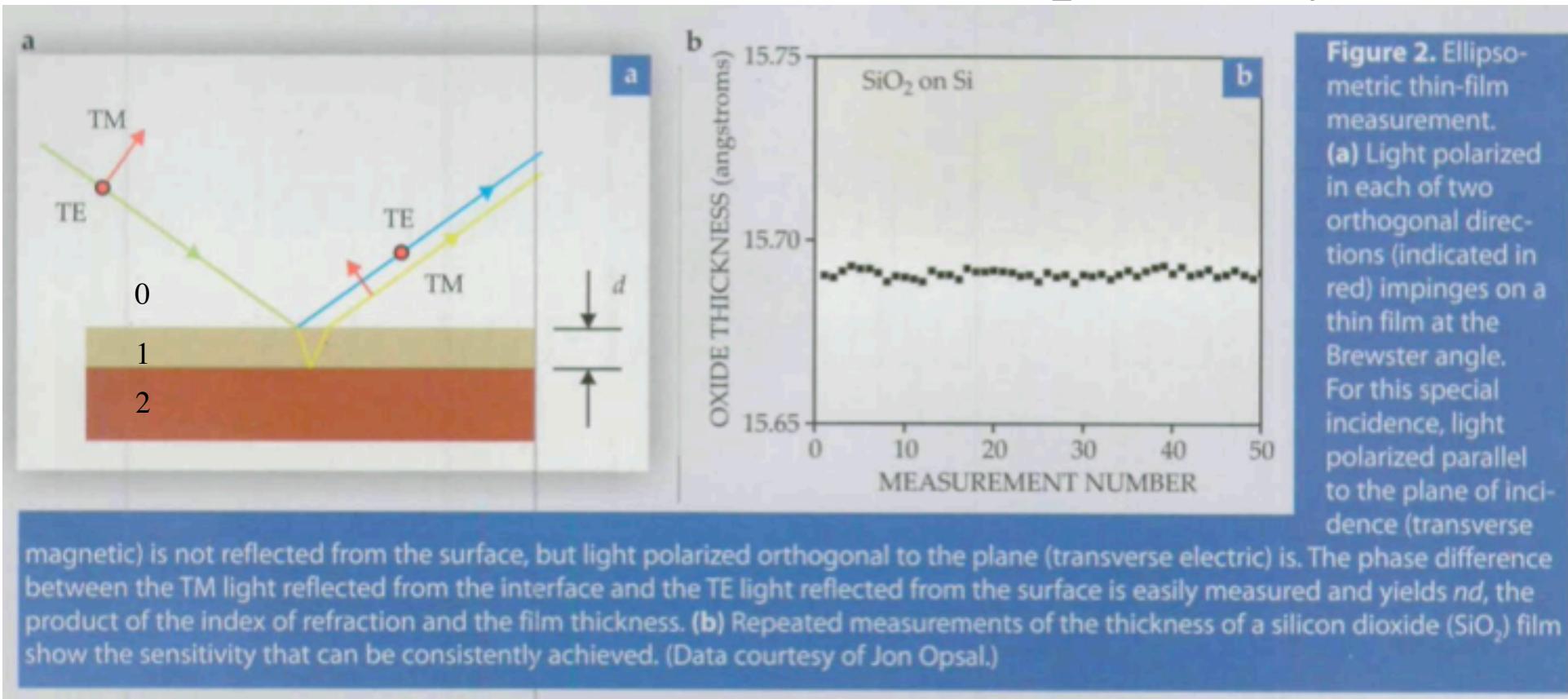
Can measure layers from 1 nm up several μm .



Principle of operation

A polarizer and a quarter wave plate which provide a state of polarization can be varied from linearly polarized light to elliptically polarized light to circularly polarized light by varying the angle of the polarizer. The beam is reflected off the layer of interest and then analyzed with the analyzer. The operator changes the angle of the polarizer and analyzer until a minimal signal is detected. This minimum signal is detected if the light reflected by the sample is linearly polarized, while the analyzer is set so that only light with a polarization which is perpendicular to the incoming polarization is allowed to pass. The angle of the analyzer is therefore related to the direction of polarization of the reflected light if the null condition is satisfied. In order to obtain linearly polarized light after reflection, the polarizer must provide an optical retardation between the two incoming polarizations which exactly compensates for the optical retardation caused by the polarization dependent reflections at each dielectric interface. Since the amplitude of both polarizations was set to be equal, the ratio of the amplitudes after reflection equals the tangent of the angle of the analyzer with respect to the normal.

Oxide characterization elipsometry

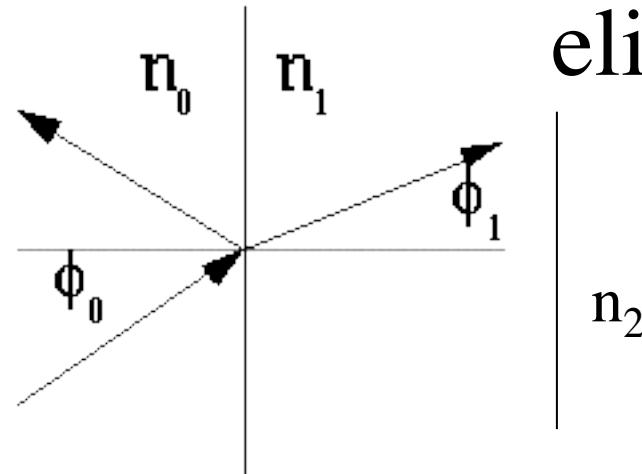


$$r_{TE} = \frac{A_{R,TE}}{A_{I,TE}} = \frac{r_{01,TE} + r_{12,TE} e^{-i\delta}}{1 + r_{01,TE} r_{12,TE} e^{-i\delta}} \quad \delta = \frac{4\pi n_1 d_1 \cos \phi_1}{\lambda}$$

$$r_{TM} = \frac{A_{R,TM}}{A_{I,TM}} = \frac{r_{01,TM} + r_{12,TM} e^{-i\delta}}{1 + r_{01,TM} r_{12,TM} e^{-i\delta}}$$

Oxide characterization

elipsometry



$$r_{TE} = \frac{A_{R,TE}}{A_{I,TE}} = \frac{r_{01,TE} + r_{12,TE} e^{-i\delta}}{1 + r_{01,TE} r_{12,TE} e^{-i\delta}}$$

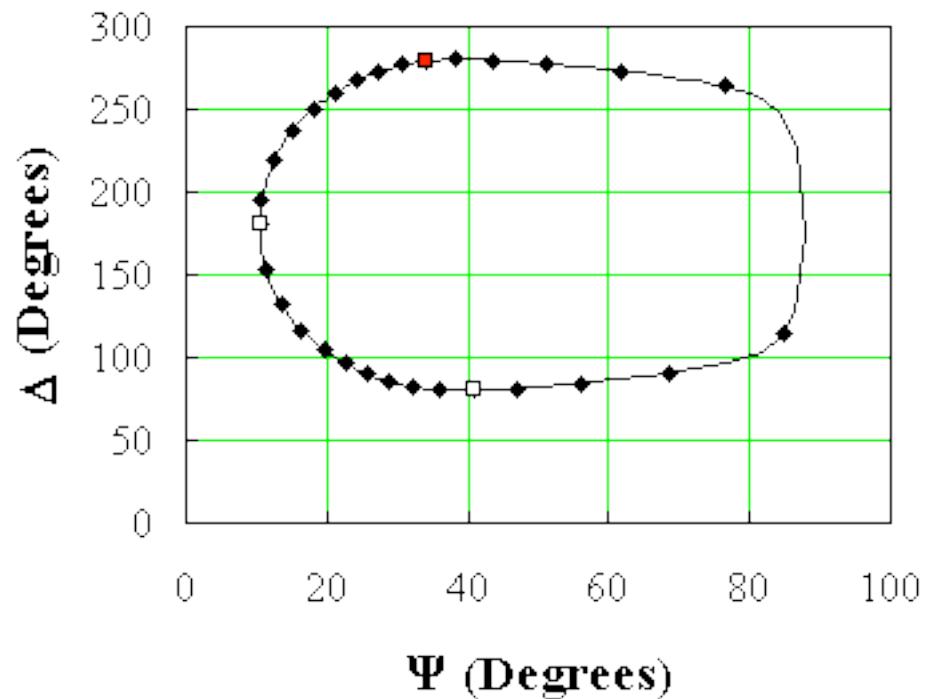
$$r_{TM} = \frac{A_{R,TM}}{A_{I,TM}} = \frac{r_{01,TM} + r_{12,TM} e^{-i\delta}}{1 + r_{01,TM} r_{12,TM} e^{-i\delta}}$$

$$\delta = \frac{4\pi n_1 d_1 \cos \phi_1}{\lambda}$$

Amplitude ratio

Phase difference

$$\frac{r_{TM}}{r_{TE}} = \tan \Psi e^{i\Delta}$$



Curves for silicon dioxide on silicon. The layer thickness increases counter clockwise from 0 (square marker on the left) in steps of 10 nm (black diamonds) and in steps of 100 nm (squares). The incident angle of the He/Ne laser beam (632.8 nm) is 70 degrees.

Breakdown stress

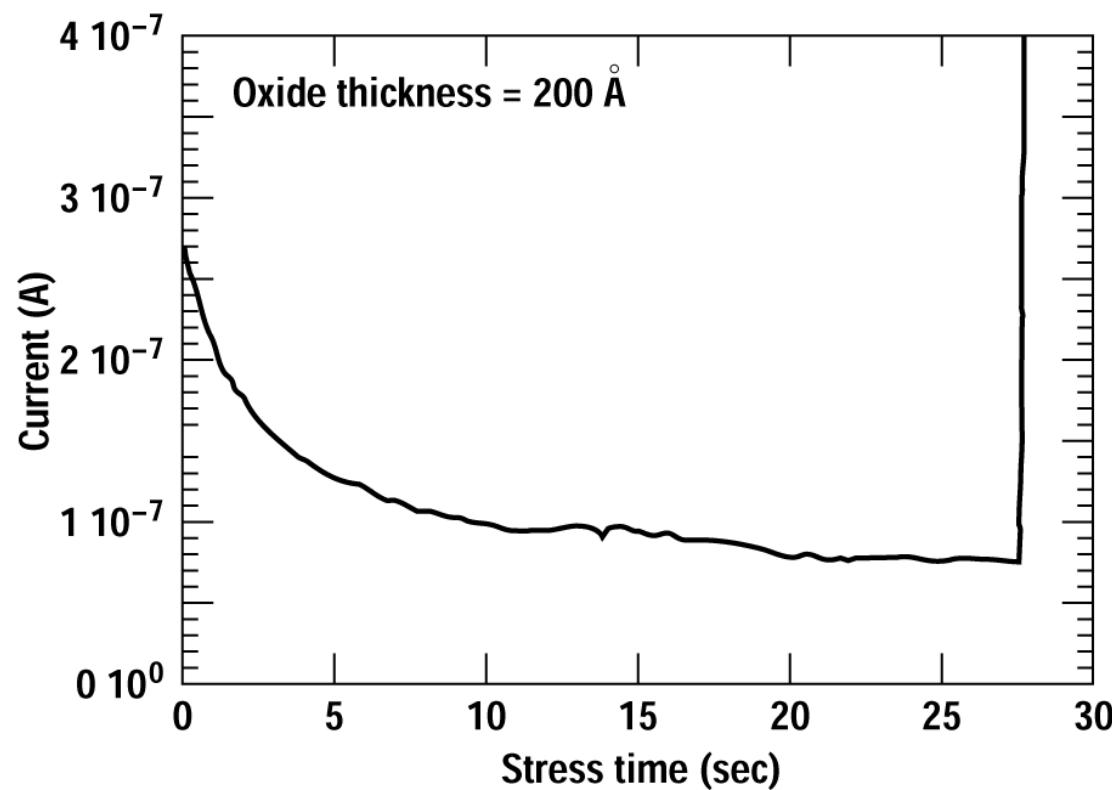


Figure 4.10 Constant voltage stress measurements of a 200-Å oxide film. The sharp increase in current near the end of the trace indicates that irreversible breakdown has occurred.

Breakdown-stress

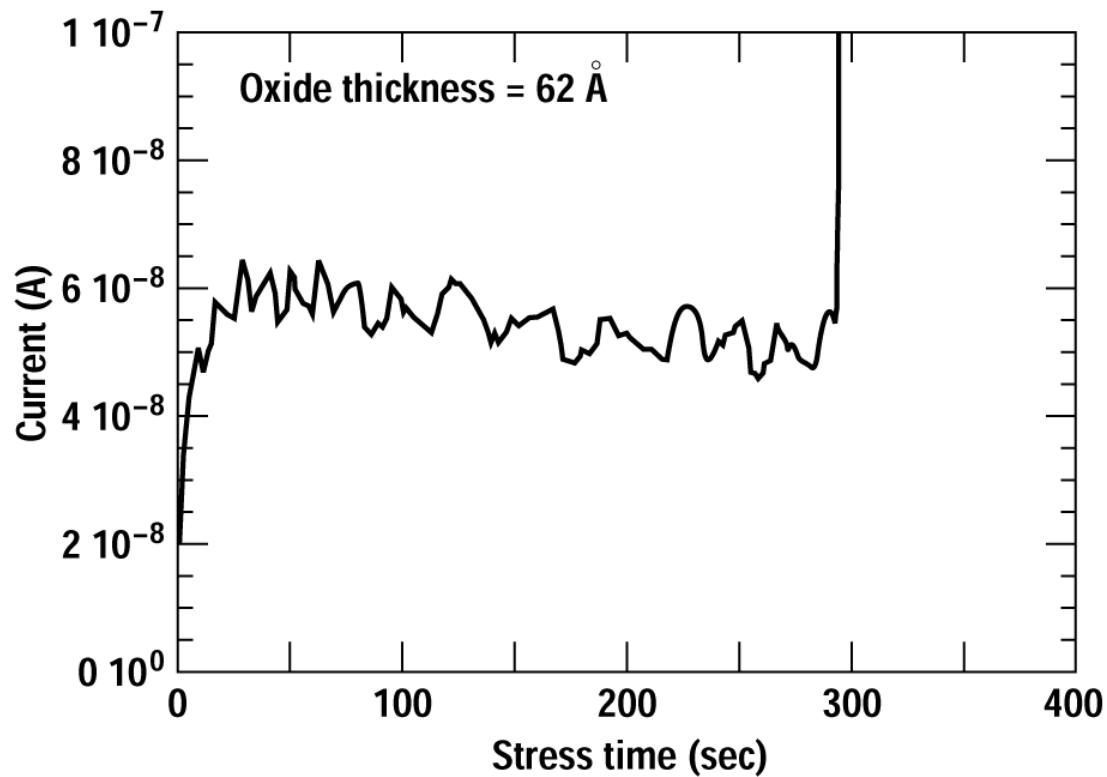


Figure 4.11 Plot similar to Figure 4.10 for a 62-Å oxide.
Note the lack of charge trapping and the low voltage
required for stressing.

Poly Si ox

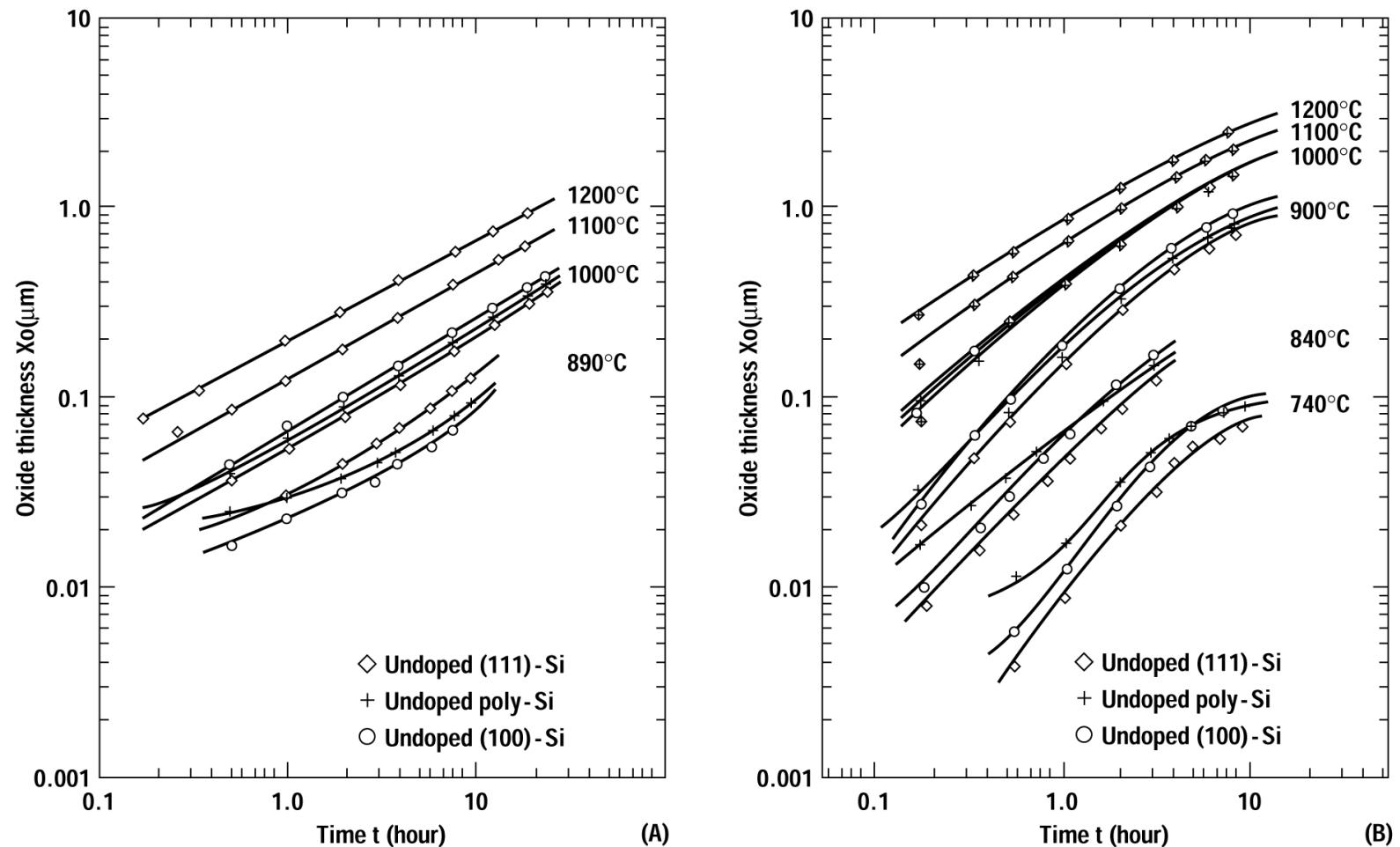
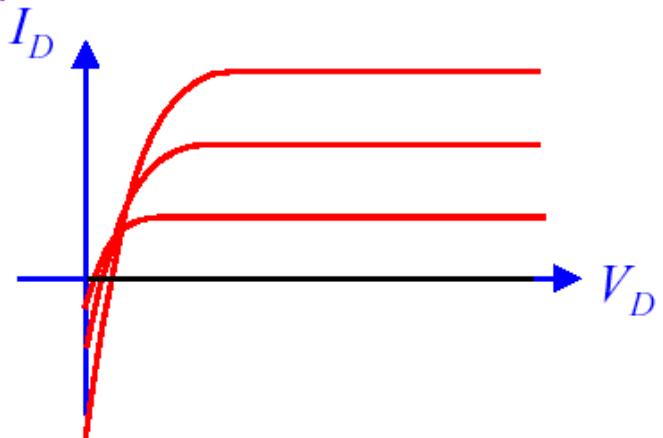


Figure 4.20 The oxidation of undoped polysilicon in (A) wet and (B) dry ambients (after Wang *et al.*, reprinted by permission, *The Electrochemical Society*).

Motivation to use high- k gate dielectric

- a practical minimum oxide thickness can be used without significant gate tunneling is about 8Å
- MOSFET with high gate leakage is more bipolar like

MOSFET characteristics with significant gate tunneling



- Need a way to increase C_{ox} without increasing leakage current

- C_{ox} is given by
$$C_{ox} = \frac{K\epsilon_0}{t_{ox}}$$

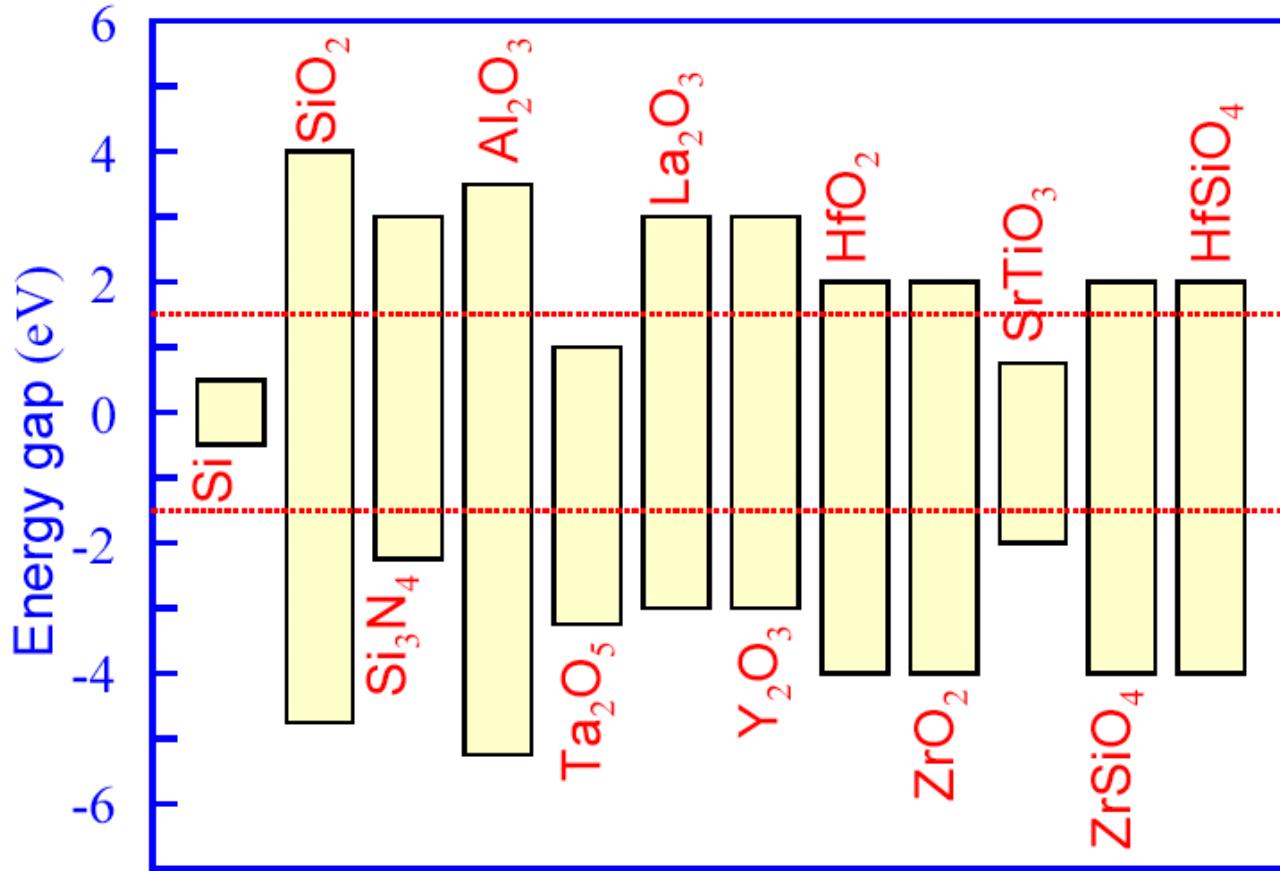
- as reducing t_{ox} is difficult, increasing k can achieve similar effects

Material requirements

- good interface quality with silicon with interface trap density $<10^{11}\text{cm}^{-3}$
- high barrier in both conduction and valance band
- good thermal stability with respect to silicon processing
- low defects in the dielectric
- usually, an ultra-thin SiO_2 layer (1-2 atomic layer) is grown before depositing the high- k dielectric

Alternative oxides

Properties of some high- k material



Alternative oxides

Dielectric	Dielectric constant	Bandgap (eV)	Conduction Band offset	Leakage reduction	Thermal stability
Silicon Dioxide (SiO_2)	3.9	9	3.5	1x	>1050°C
Silicon Nitride (Si_3N_4)	7	5.3	2.4	?	>1050°C
Aluminum Oxide (Al_2O_3)	~10	8.8	2.8	$10^2\text{-}10^3$ x	~1000°C RTA
Tantulum Pentoxide (Ta_3O_5)	25	4.4	0.36	?	unstable with Si
Lanthanum Oxide (La_2O_3)	~21	6	2.3	?	?
Gadolinium Oxide (Gd_3O_3)	~12	?	?	?	?
Yttrium Oxide (Y_2O_3)	~15	6	2.3	$10^4\text{-}10^5$ x	Form silicate
Hafnium Oxide (HfO_2)	~20	6	1.5	$10^4\text{-}10^5$ x	~950°C
Zirconium Oxide (ZrO_2)	~23	5.8	1.4	$10^4\text{-}10^5$ x	~900°C
Strontium Titanate (SrTiO_3)		3.3	-0.1	?	?
Zirconium Silicate (ZrSiO_4)		6	1.5	?	?
Hafnium Silicate (HfSiO_4)		6	1.5	?	?

Oxidation furnace

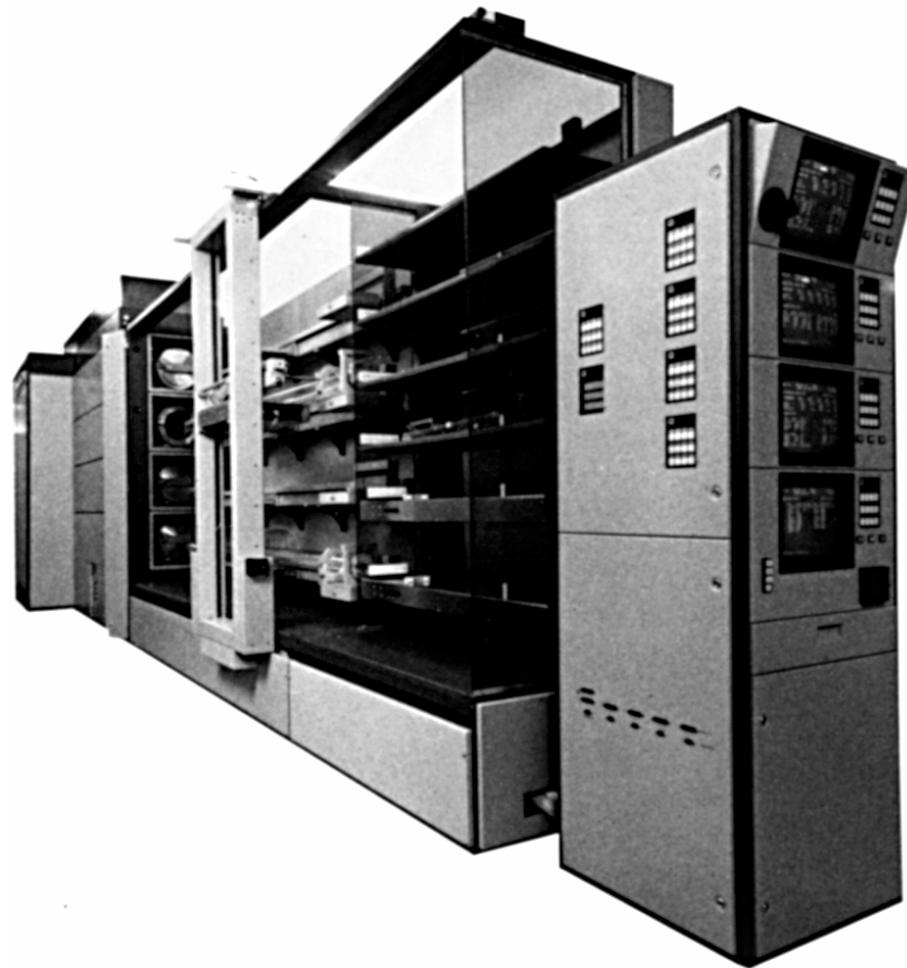


Figure 4.24 Horizontal tube oxidation/diffusion system includes computer controller, load station, and four tubes (*photo courtesy of ASM International*).

Oxidation furnace

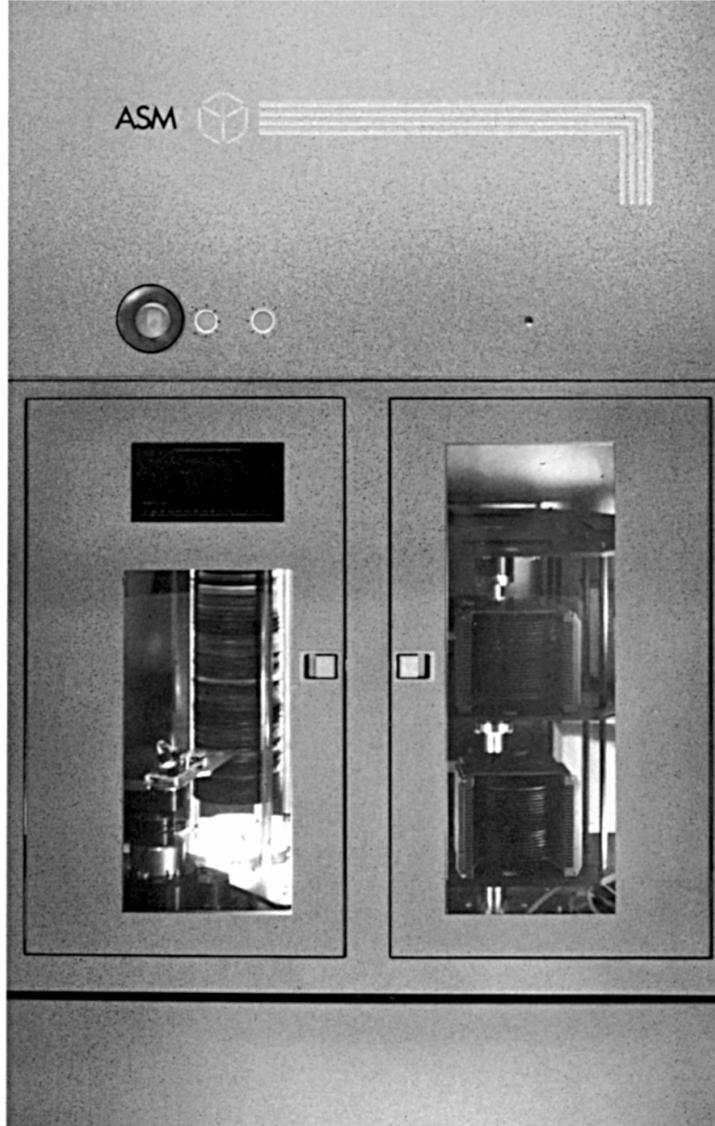


Figure 4.26 Vertical oxidation system showing carousel, robot arm, and wafers about to be raised into the furnace (*photo courtesy of ASM International*).