6: Oxidation – Film deposition

→ models from Sze
→ Qualitative information from Wolf (very good!)

To fabricate devices and integrated circuits thin films are needed. (see picture of MOSFET)

→ insulating oxide thin films → important for field and gate oxides.

→ Ability to make smooth, (native) insulating oxide is KEY to Si device performance

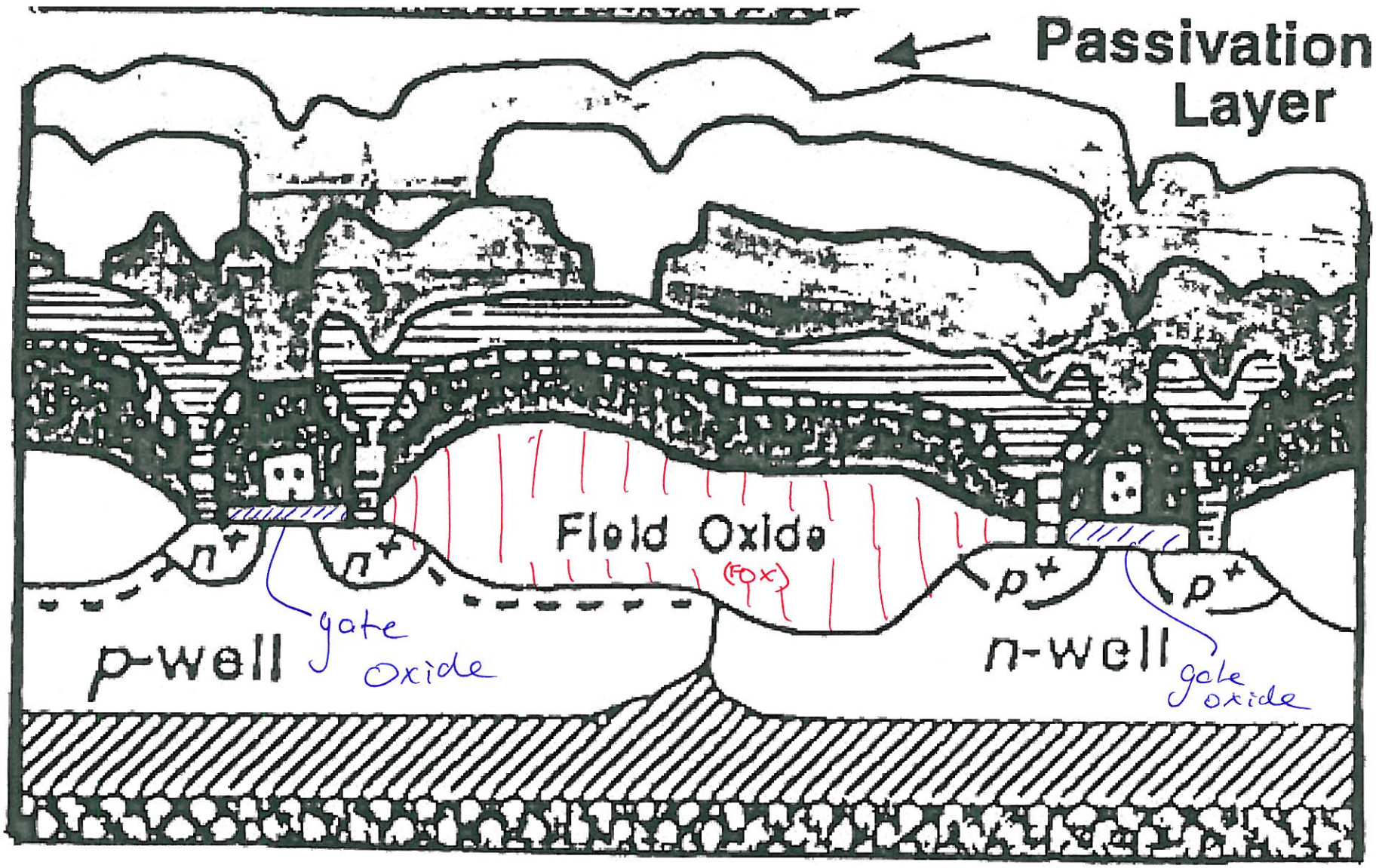
↑ Si/SiO_2 can also be made to have few defects, i.e. a low S.R.V

→ GaAs does have this property

Several ways to grow oxide:

1. Thermal oxidation ← most important technologically
2. Electrochemical Anodization ← (Silicon can be anodized as can aluminum → alumina)
3. Plasma Reaction → O_2 plasma oxidation.

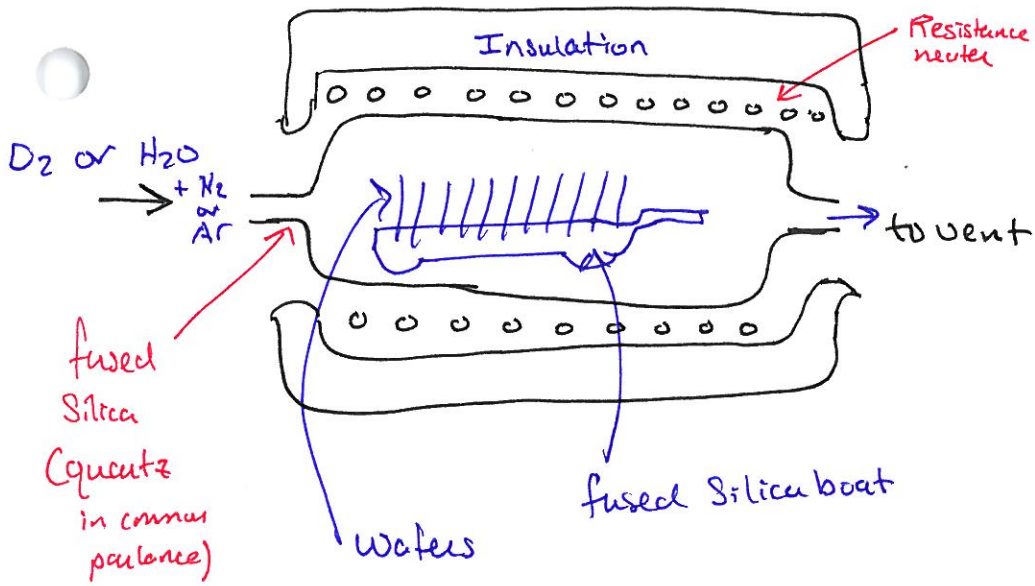
Oxides and other insulators can also be deposited by physical vapor or chemical vapor deposition routes, which we will cover latter



Fox → for isolation of n and p devices.

6.01

Thermal Oxidation



- Kinetics of Growth SZE (11.1.1)

$$Si(s) + O_2(g) \longrightarrow SiO_2(s) \quad \text{"Dry" oxidation}$$

$$Si(s) + 2H_2O(g) \longrightarrow SiO_2(s) + 2H_2(g) \quad \text{"Wet oxidation"}$$

→ $Si - SiO_2$ interface moves into wafer.

→ Surface contamination stays on top of grown oxide.

Ex. If you grow SiO_2 layer 100 nm thick, how much Si do you consume?

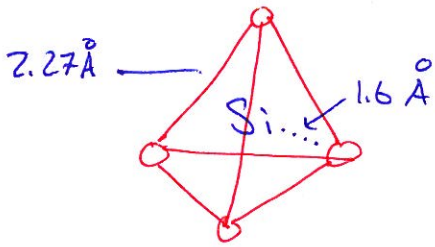
$$t_{Si} = 0.44\, t_{SiO_2} \quad (\text{thickness} = t)$$

$$\text{Volume of } 1\text{ mol Si} = \frac{\text{mw Si}}{\text{Density Si}} = \frac{28.09\ g/mol}{2.33\ g/cm^3} = 12.06\ cm^3/mol$$

$$\text{Volume } 1\text{ mol } SiO_2 = \frac{\text{mw } SiO_2}{\text{Density } SiO_2} = \frac{60.08\ g/mol}{2.21\ g/cm^3} = 27.18\ cm^3/mol$$

$$\frac{\text{Thickness Si} \times \text{Area}}{\text{Thickness } SiO_2 \times \text{Area}} = \frac{\text{Volume/mol Si}}{\text{Volume/mol } SiO} = \frac{12.06}{27.18} = \boxed{0.444}$$

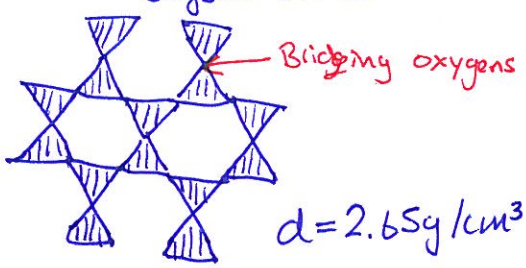
Structure of SiO_2



Basic structural unit is Si surrounded tetrahedrally by 4 O atoms

Tetrahedra are joined together at their corners by oxygen bridges → various SiO_2 (silica) phases.

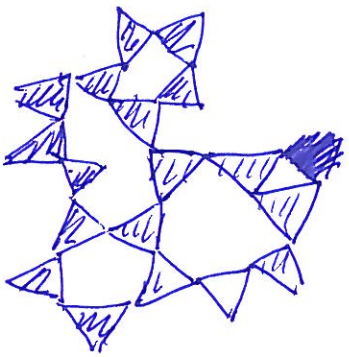
2d "Quartz" crystal structure



$d = 2.65 g/cm^3$

(see crystal maker for actually more complex crystal structure)

Amorphous Silica



No long range order

$d \sim 2.21 g/cm^3$

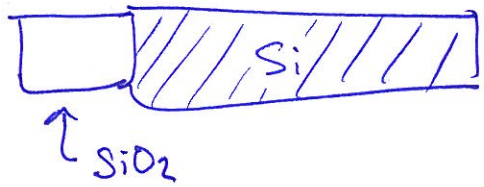
impurities, eg Na, can be incorporated and diffuse quickly

Pure SiO → Fused Silica

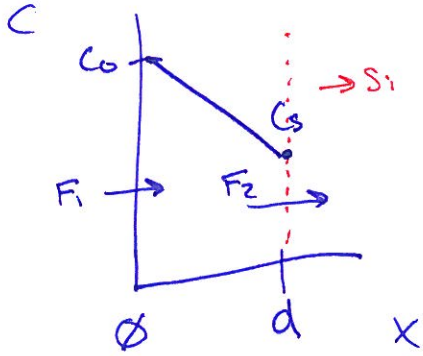
→ this is often called "quartz" but is actually amorphous!

Kinetics of Thermal Oxidation (Deal Grove Model

Basic Model



Q: wet faster than Dry?
Any hypotheses?
What factors do you think could affect rate?



C_0 = surface concentration of oxidant (O_2 or H_2O)

depends on T, P but <u>not flow</u>

$$F_1 = D\frac{\partial c}{\partial x} \cong \frac{D(C_0 - C_s)}{x}$$

assuming linear concentration gradient

x → thickness of oxide layer present

at Si surface

$$F_2 = K C_s$$

(assume rate is ∝ to C_s)

K → surface reaction rate constant for oxidation

at steady state: $\boxed{F_1 = F_2 = F}$

(meaning at some condition dictated by the growth conditions)

$$F = \frac{D(C_o - C_s)}{x}$$

$$F = k C_s$$

combine

$$F = \frac{D C_o}{x} - \frac{D F}{k x}$$

$$F\left(1 + D/kx\right) = \frac{D C_o}{x}$$

$$\boxed{F = \frac{D C_o}{x + D/k}}$$

Let C_1 = # of Molecules of oxidizing species / unit Volume in Oxide

→ $\boxed{2.2 \times 10^{22} \ SiO_2 \text{ "Molecules"} / cm^3 \text{ in oxide}}$

in growing oxide then need $\boxed{\begin{array}{l} 2.2 \times 10^{22} \ O_2 \text{ molecules}/cm^3 \\ \text{or } 4.4 \times 10^{22} \ H_2O \text{ molecules}/cm^3 \end{array}}$

therefore the growth rate of the oxide layer thickness

Flux ~~rate~~ of molecules coming in (units $\frac{\text{molecules}/cm^2}{\text{unit time}}$)

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

# of molecules per unit volume (cm^3)

Can solve dif EQ: w/ initial conditions

$$x(\emptyset) = d_o$$

↑ time = $\emptyset$

(or d_o is thickness in earlier growth step)

$$\int_{d_o}^{x} x + \frac{D}{K}\, dx = D\frac{C_o}{C_1}\int_{\emptyset}^{t} dt$$

$$\left| \frac{x^2}{2} + \frac{D}{K}x \right|_{d_o}^{x} = D\frac{C_o}{C_1}(t) +$$

$$\left(\frac{x^2}{2} + \frac{D}{K}x\right) - \left(\frac{d_o^2}{2} + \frac{D}{K}d_o\right) = D\frac{C_o}{C_1}(t)$$

get rid of the 2 by multiplying all by 2

$$\cancel{2}\frac{x^2}{\cancel{2}} + 2\frac{D}{K}x = 2D\frac{C_o}{C_1}t + \left(\frac{2d_o^2}{2} + \frac{2D}{K}d_o\right)$$

$$\boxed{\text{Define } \tau = \frac{C_i\left(d_o^2 + \frac{2D}{K}d_o\right)}{2C_oD}}$$

$$\Rightarrow \quad x^2 + \frac{2D}{K}x = \frac{2DC_o}{C_1}(t + \tau)$$

diffusion coefficient of

surface concentration

↑ time

rate constant for reaction at the Si-SiO2 surface

Molecules oxidizing species per unit volume

Solve for x using quadratic formula

$$\boxed{x = \frac{D}{k}\left[\left(1 + \frac{2C_0k^2(t+\tau)}{DC_1}\right)^{1/2} - 1\right]}$$

aside...

$$x = \frac{-b - \sqrt{b^2 - 4ac}}{2a}$$

derived from completing square, ie factoring.

plug in here

* Now we explore limiting cases/ ~~other~~ regimes

to do this we expand $\left[1 + \frac{2C_0k^2(t+\tau)}{DC_1}\right]^{1/2} = f(t) \cong f(0) + f'(0)(u) = 1 + \frac{C_0k^2}{CD_1}u = 1 + \frac{C_0k^2}{CD}(t+\tau)$

expand about $t+\tau = u$

$f'(u) = \frac{\cancel{2}C_0k^2}{\cancel{2}DC_1}\left(1 + \frac{2C_0k^2u}{DC_1}\right)^{-1/2}$

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

see below

for t is small:

$$x \approx \frac{C_0}{C_1}k(t+\tau)$$

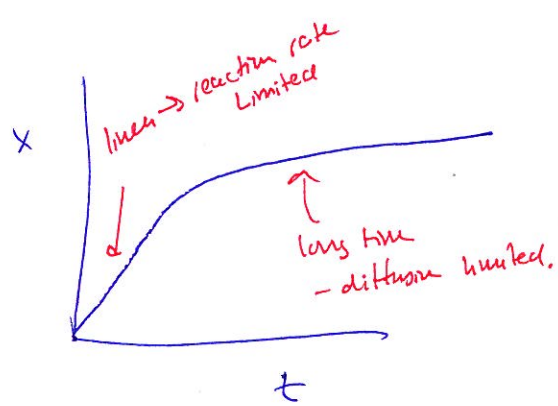
(this comes from ~~tag~~ ignoring the squared terms from eqn on previous page)

for t is large:

→ take full expression and eliminate 1 and −1 or ignore the linear term!

$$\boxed{x \cong \sqrt{\frac{2DC_0(t+\tau)}{C_1}}} \rightarrow \boxed{x^2 = B(t+\tau)}$$

see below



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

$$A = \frac{2D}{k} \qquad B = \frac{2DC_0}{C_1}$$

parabolic rate constant

$$B/A = kC_0/C$$

→ Linear rate constant

Experimentally measured values agree well with the measured results.

Fit to experimental data.

a. for wet oxidation d_0 is very small (when no oxide already present)

b. for dry oxidation $d_0 \sim 200\text{Å}$ (implying that for thin oxides the model breaks down as discussed below)

Temperature Dependence

linear rate constant (short time) B/A varies as $\boxed{\exp -E_a/kT}$ $\Rightarrow$ w/ $E_a \sim 2eV$

ΔH Si-Si bond $\rightarrow$ $\boxed{1.83\ eV}$

$\rightarrow$ consistent w/ both wet and dry being reaction-rate limited in the linear regime by activation of the Si surface.

(also rate constant orientation-dependent)

Si 111 faster than Si 100

Why? (higher density of surface atoms)

T- dependence of parabolic rate constant, B

$$\Rightarrow \sim \exp(-E_a/kT)$$

$E_{a,\,dry} = 1.24\,eV$ $\quad$ $E_{a,\,wet} = 0.71\,eV$

Why different? ask class for hypothesis

→ Data from independent diffusion measurements in fused Silica

different diffusing species

$E_{a,\,diffusion\ O_2} = 1.18\,eV$

$E_{a,\,diffusion\ H_2O} = 0.79\,eV$

exact mechanism not precisely understood. → H_2O is smaller than O_2 ... diffuses faster?

→ H_2O more polar ↑ non polar

SiO_2 is highly polar lattice...

→ Crystal ~~orie~~ orientation dependence?

(No! does not depend on Si, only amorphous SiO_2 properties)

Dry oxide ~~[illegible]~~ → higher quality

Wet oxide → residual proton content, higher ionic mobility, current leakage, etc.

thin oxides (gate oxides) → dry oxidation

thick oxides (field oxide) → wet oxidation

Thin Oxide growth

Simple model below not suitable as rapid growth is observed to $d_0 \sim 20\,nm$.

but... gate oxides < 10 nm...

growth mechanism

→ early stages of growth, large compressive stress in oxide layer → reduces O_2 diffusion coefficient → See 8.4.1 Wolf for discussion of other mechanisms → NOT Resolved!!!

→ the $D \to D_{bulk}$ as film grows due to viscous flow for glass layer

for $x^2 + Ax = B(t+\tau)$ → $\boxed{x^2 = B(t+\tau)}$

↳ $A = 2D/k$ if D is small, ignore

$B\tau = d_0^2 + \boxed{2Dd_0/k}$ → again small for small/short times

so $\boxed{x^2 - d_0^2 = Bt}$

and d_0 is approximated by

$$\boxed{d_0 = \sqrt{B\tau} = \sqrt{\frac{2DC_0}{C_1}\tau}}$$

⇒ based on these assumptions, initial growth should follow a parabolic form

think about molecules

Dopant redistribution

$$m = C_{Si} / C_{SiO_2}$$

Ratio of eq. conc. impurity in each material

* Oxides take up impurity ($m < 1$)

(Boron)

* Oxides reject impurity ($m > 1$)

(Phosphorus + Gallium)

→ ~~adsorb~~ Final dopant distribution depends on diffusion through oxide in Si, and on $\underline{\underline{m}}$.

Other factors which affect oxidation Rate:

Dopant Effects → $\boxed{B, P, As}$ → enhance oxidation rate when present at high concentrations

Why?

B → dopant piles up in oxide, → weak structure, (m<1, pickup oxide)
as B 3- coordinate, faster O_2 diffusion
(not observed for Ga or Al...
also in oxide... diffuse away from interface?)

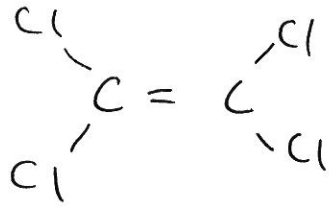
→ still seems like empirical understanding.
→ affects parabolic rate constant and hence implies diffusion

P → m>1 → piles up in Si surface
→ only affects linear rate constant
& implies mechanism related to reaction rate constant, K

→ Si E_f shifts → more vacancies?

Chlorine Additives

Cl_2, HCl, or



① removes impurities (volatilizes metals) as chlorides

② Improves oxide quality: + dielectric breakdown strength
+ lowers interfacial trap density

Effects of Pressure on Oxidation Rates

Deal-Grove model predicts

<u>linear</u> dependence on the B and B/A

constants on the Oxygen ~~partial~~ pressure.

Because:

C_0 = surface concentration of oxidant $\propto P$

C_0 is in both B and B/A

Reality: $B/A \propto P$

$B \propto P^{0.1-0.8}$

⇒ model and assumptions not perfect! Engineers use as starting point.

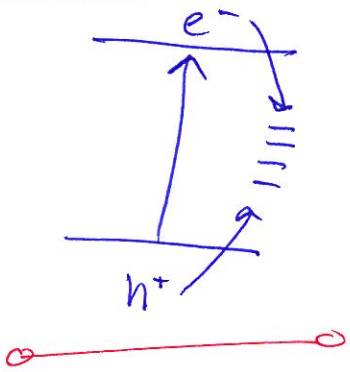
High pressure → thick thermal high quality oxides

Low Pressure → thin oxides → precisely control Rate

(8.5 Wolf) Si - SiO_2 interface

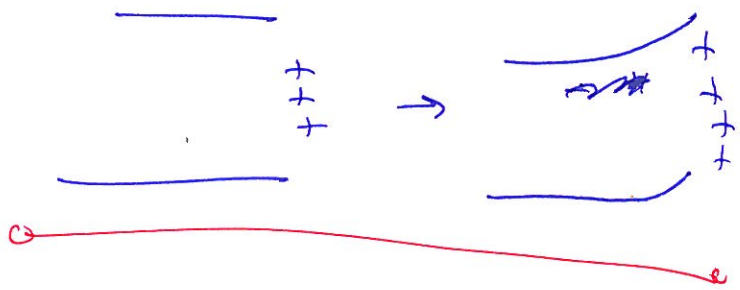
→ charge and defects (traps) $\boxed{\text{Critical}}$ to device performance (MOSFET, Solar Cell, etc...)

interface traps * Draw examples from below after list



or

Electric field!



→ Measured using electrical devices

$\boxed{\text{MOS Capacitor}}$

Metal, Oxide, Semiconductor

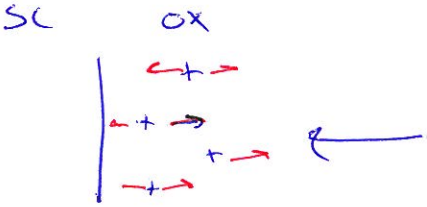
Charge:

(1) Fixed oxide charge, Q_f (C/cm^2)

What could this be?

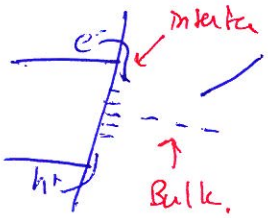
* excess cations (Si^{4+}) or anions (O^{2-})

Kinetically trapped



(2) Mobile ionic charge, Q_m, (C/cm^2)

(ionized alkali metals, Na^+, K^+, etc



(3) Interface traps (Q_{it} (C/cm^2)) or D_{it} #/$cm^2 \cdot eV$

H_2 anneal → diffuses into SiO_2, reacts w/ Dangling Si surface bonds v. imp. for PV!

(4) Oxide trapped charge → charge in bulk oxide, neutral until filled w/ e^- or h^+

Oxidation Systems (8.12 wolf)

① Thermal Budget → $\int T(t)\,dt$

→ dopants move at high Temp. → smear out desired profiles.

→ Engineers must consider Thermal Budget.

② Thermal Process Tools

a. * hot-wall horizontal furnace

b. → * vertical furnace (better heat uniformity Radially because heat rises!)

(also improved particle control)

c. Rapid Thermal Annealer (RTA) → RT → 1100°C in Seconds!

① reduced thermal budget (fast ramp + cool)

② single wafer process. (like rest of fab) etc...

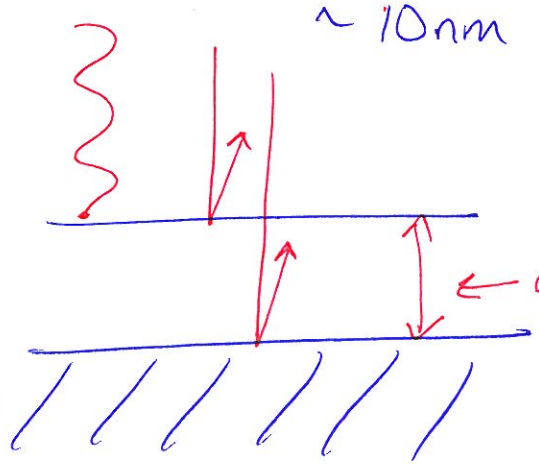
Atmospheric and low Pressure furnaces

Measurement of Oxide thickness

→ Many ways!

→ easy: optical interference (oxides are colored why?)

~ 10nm to ~ 1000nm



← destructive and constructive interference!

order of interference

phase shift $P = \phi_s - \phi_f$

ϕ_s → phase Si/SiO2

ϕ_f → phase Si/SiO2

$$x_{ox} = \lambda \left(g - P \right) / 2n^*$$

$$n^* = \left(n_1^2 - \sin^2 \theta \right)^{1/2}$$

angle of incidence

next year → look up derivation of these equations.