EE 143
Microfabrication Technology
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Prof. Clark T.-C. Nguyen

Dept. of Electrical Engineering & Computer Sciences
University of California at Berkeley
Berkeley, CA 94720

Lecture Module 2: Oxidation

Oxidation

Thermal Oxidation of Silicon

- Achieved by heating the silicon wafer to a high temperature (~900°C to 1200°C) in an atmosphere containing pure oxygen or water vapor
- Enabling reactions:

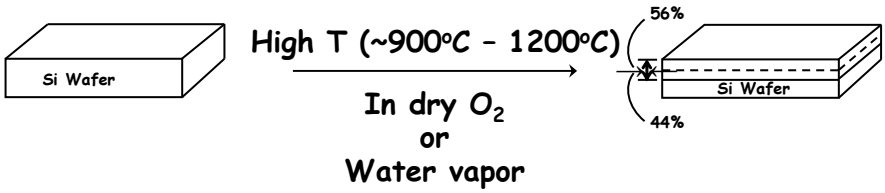
For dry oxygen:

$Si + O_2 \rightarrow SiO_2$

For water vapor:

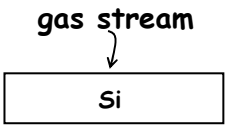
$Si + 2H_2O \rightarrow SiO_2 + 2H_2$

Schematically:



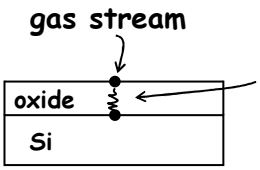
Oxidation Modeling

(1) Initially: (no oxide @ surface)



↳ Growth rate determined by reaction rate @ the surface

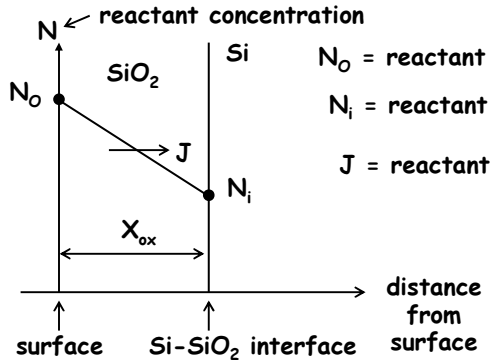
(2) As oxide builds up:



Reactant must diffuse to Si surface where the oxidation reaction takes place

↳ Growth rate governed more by rate of diffusion to the silicon-oxide interface

Oxidation Modeling (cont.)



N_O = reactant conc. at oxide surface [in cm^{-2}]

N_i = reactant conc. at Si-SiO_2 interface

J = reactant flux = $-D\dfrac{\partial N(x,t)}{\partial x}$ [Fick's 1st Law of Diffusion]

Diffusion coeff. [in μm/hr or m/s]

In the SiO_2:

$$J = D\frac{(N_O - N_i)}{X_{OX}} = \text{constant} \qquad (1)$$

[in # particles/(cm^2·s)]

Assumption that the reactant does not accumulate in the oxide.

Oxidation Modeling (cont.)

At the Si-SiO_2 interface:

Oxidation rate $\propto N_i$ $\therefore$ $J \propto N_i$ $\Longrightarrow$ $J = k_s N_i$ (2)

Reaction rate constant @ Si-SiO_2 interface

Combining (1) and (2):

$$\left[N_i = \frac{J}{k_s}\right] \Rightarrow J = D\left(\frac{N_O - J/k_s}{X_{OX}}\right)$$

$$JX_{OX} = DN_O - \frac{DJ}{k_s} \rightarrow J\left(X_{OX} + \frac{D}{k_s}\right) = DN_O$$

$$\therefore \quad J = \frac{DN_O}{X_{OX} + \frac{D}{k_s}} = \text{Flux of reactants}$$

Oxidation Modeling (cont.)

Find an expression for $X_{OX}(t)$:

oxidizing flux

Rate of change of oxide layer thickness w/time $\Big\} = \dfrac{dX_{OX}}{dt} = \dfrac{J}{M} = \dfrac{DN_O/M}{X_{OX} + D/k_s}$ (3)

# of molecules of oxidizing species incorporated into a unit volume of oxide $\Big\} \begin{array}{l} = 2.2\times10^{22} cm^{-3} \text{ for } O_2 \\ = 4.4\times10^{22} cm^{-3} \text{ for } H_2O \end{array}$

Solve (3) for $X_{OX}(t)$: [Initial condition $X_{OX}(t=0) = X_i$]

$$\frac{dX_{OX}}{dt} = \frac{DN_O/M}{X_{OX} + D/k_s} \quad \Rightarrow \quad \int_{X_i}^{X_{OX}} \left(X_{OX} + \tfrac{D}{k_s}\right) dX_{OX} = \int_0^t \frac{DN_O}{M}\, dt$$

Oxide Thickness Versus Time

Result:

additional time required to go from $X_i \rightarrow X_{OX}$

time required to grow X_i [X_i = initial oxide thickness]

$$X_{OX}(t) = \frac{A}{2}\left\{\left[1 + \frac{4B}{A^2}(t+\tau)\right]^{1/2} - 1\right\}$$

where $A = \dfrac{2D}{k_s}$ $\qquad \tau = \dfrac{X_i^2}{B} + \dfrac{X_i}{(B/A)}$

$B = \dfrac{2DN_O}{M}$ $\qquad D = D_O \exp\left(-\dfrac{E_A}{kT}\right)$

[i.e., D governed by an Arrhenius relationship → temperature dependent]

Oxidation Modeling (cont.)

For shorter times:

$$\left[(t+\tau) << \frac{A^2}{4B}\right] \Rightarrow X_{OX}(t) = \underbrace{\left(\frac{B}{A}\right)}_{\text{linear growth rate constant}}(t+\tau) \Rightarrow$$

oxide growth limited by reaction at the Si-SiO_2 interface

Taylor expansion (first term after 1's cancel)

For long oxidation times: oxide growth diffusion-limited

$$\left[(t+\tau) >> \frac{A^2}{4B}\right] \Rightarrow X_{OX}(t) = \sqrt{B(t+\tau)} \approx \sqrt{Bt}$$

$t >> \tau$

Parabolic rate constant

Oxidation Rate Constants

Table 6–2 Rate constants describing (111) silicon oxidation kinetics at 1 Atm total pressure. For the corresponding values for (100) silicon, all C_2 values should be divided by 1.68.

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

- Above theory is great … but usually, the equations are not used in practice, since measured data is available
  - Rather, oxidation growth charts are used

Oxidation Growth Charts

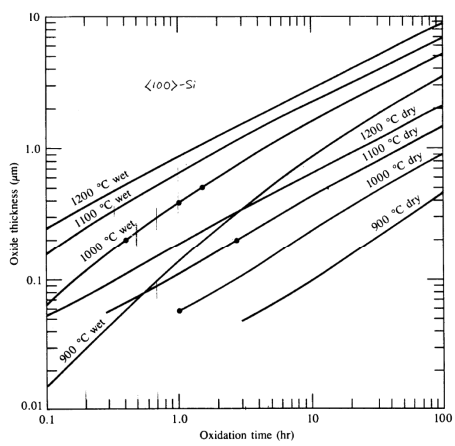


Fig. 3.1

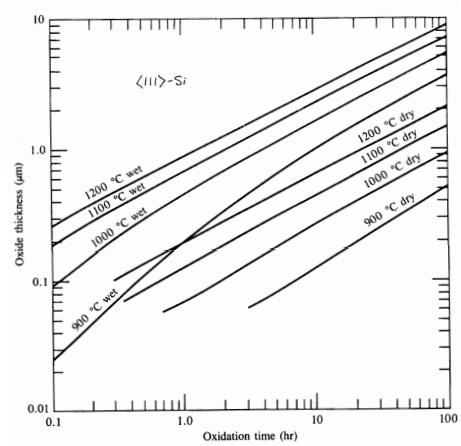


Fig. 3.2

Using the Oxidation Growth Charts

Example:

- <100> silicon
- Starting oxide thickness: X_i=100nm
- Want to do wet oxidation @ 1000°C to achieve X_{ox}=230nm
- What is the time *t* required for this?

Growth Chart for <100> Silicon

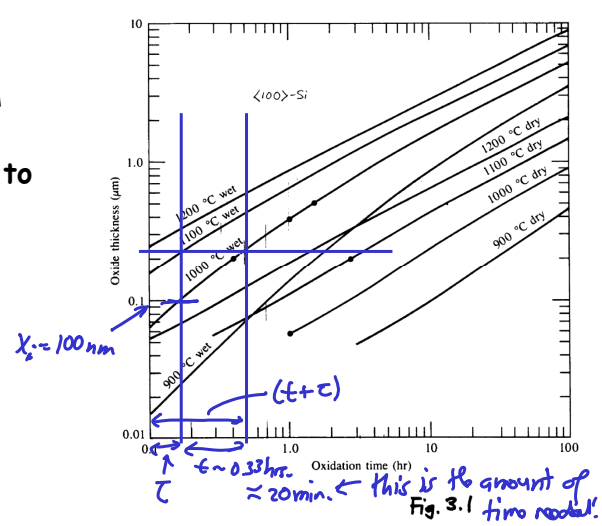


Fig. 3.1

Factors Affecting Oxidation

- In summary, oxide thickness is dependent upon:
  1. Time of oxidation
  2. Temperature of oxidation
  3. Partial pressure of oxidizing species ($\propto N_o$)
- Also dependent on:
  4. Reactant type:
     Dry O_2
     Water vapor ⇨ faster oxidation, since water has a higher solubility (i.e., D) in SiO_2 than O_2
  5. Crystal orientation:
     <111> ← faster, because there are more bonds available at the Si-surface
     <100> ← fewer interface traps; smaller # of unsatisfied Si-bonds at the Si-SiO_2 interface

Factors Affecting Oxidation

6. Impurity doping:
   P: increases linear rate const.
      no affect on parabolic rate constant
      faster initial growth → surface reaction rate limited
   B: no effect on linear rate const.
      increases parabolic rate const.
      faster growth over an initial oxide → diffusion faster

Dopant Redistribution During Oxidation

- This must be considered and designed for when generating any process flow, especially for transistor circuits, e.g., CMOS
- During oxidation, the impurity concentration at the Si-SiO_2. interface can increase (pile-up) or deplete, depending upon the dopant type
- Whether a particular impurity depletes or piles up @ the interface depends on:
  1. Diffusion coefficient, D (of the impurity in SiO_2)
  2. Segregation coefficient, m:

$$m = \frac{\text{impurity equil. conc. in Si}}{\text{impurity equil. conc. in } SiO_2}$$

Dopant Behavior During Oxidation

- Segregation coefficient (m) and diffusion constant (D) combine to determine dopant behavior during oxidation:

Impurity	m	D in SiO_2	Dopant Behavior During Oxidation
B	<0.3 (small)	Small	depl. f/Si surface, pile up in oxide
B (oxidation w/H_2)	<0.3 (small)	Large	depl. f/Si surface, depl. from oxide
P, Sn, As	~10 (large)	Small	pile up in Si, very little diff. into SiO_2
Ga	20 (large)	Large	depl. f/Si, depl. from oxide

e.g., wet oxidation where H_2 is present as a by-product.

So large that it depletes the dopant @ the Si surface despite

Dopant Redistribution During Oxidation