

EE 143
Microfabrication Technology
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Lecture Module 2: Oxidation

EE 143: Microfabrication Technology LecM 2 C. Nguyen 2/14/10 1



Oxidation

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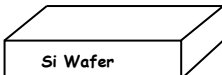
Thermal Oxidation of Silicon

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- 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:

<u>For dry oxygen:</u>	<u>For water vapor:</u>
$\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2$	$\text{Si} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{H}_2$

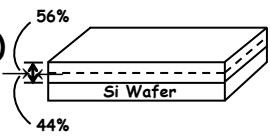
Schematically:



Si Wafer

High T (~900°C - 1200°C)

In dry O₂
or
Water vapor




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Oxidation Modeling

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(1) Initially: (no oxide @ surface)

gas stream




Si

↪ Growth rate determined by reaction rate @ the surface

(2) As oxide builds up:

gas stream



oxide

Si

↪ 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

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Oxidation Modeling (cont.)

N_o = reactant conc. at oxide surface [in cm^{-2}]
 N_i = reactant conc. at Si-SiO₂ interface
 J = reactant flux = $-D \frac{\partial N(x,t)}{\partial x}$ [Fick's 1st Law of Diffusion]
 Diffusion coeff. [in $\mu\text{m/hr}$ or m/s]
 distance from surface

In the SiO₂:

$$J = D \frac{(N_o - N_i)}{X_{ox}} = \text{constant} \quad (1)$$

[in # particles/(cm²·s)] Assumption that the reactant does not accumulate in the oxide.

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Oxidation Modeling (cont.)

At the Si-SiO₂ interface:
 Oxidation rate $\propto N_i \therefore J \propto N_i \Rightarrow J = k_s N_i \quad (2)$
 Reaction rate constant @ Si-SiO₂ interface

Combining (1) and (2):

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

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

$$\therefore J = \frac{DN_o}{X_{ox} + \frac{D}{k_s}} = \text{Flux of reactants}$$

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Oxidation Modeling (cont.)

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

oxidizing flux

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

of molecules of oxidizing species incorporated into a unit volume of oxide } $= 2.2 \times 10^{22} \text{ cm}^{-3}$ for O_2
 $= 4.4 \times 10^{22} \text{ cm}^{-3}$ for H_2O

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

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

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Oxide Thickness Versus Time

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

$B = \frac{2DN_o}{M}$ $D = D_o \exp\left(-\frac{E_A}{kT}\right)$

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

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Oxidation Modeling (cont.)

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For shorter times:

$$\left[(t + \tau) \ll \frac{A^2}{4B} \right] \Rightarrow X_{OX}(t) = \underbrace{\left(\frac{B}{A} \right)}_{\text{linear growth rate constant}} (t + \tau) \Rightarrow \text{oxide growth limited by reaction at the Si-SiO}_2 \text{ interface}$$

Taylor expansion (first term after 1's cancel)

For long oxidation times: oxide growth diffusion-limited

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

$t \gg \tau$ Parabolic rate constant

EE 143: Microfabrication Technology LecM 2 C. Nguyen 2/14/10 9

Oxidation Rate Constants


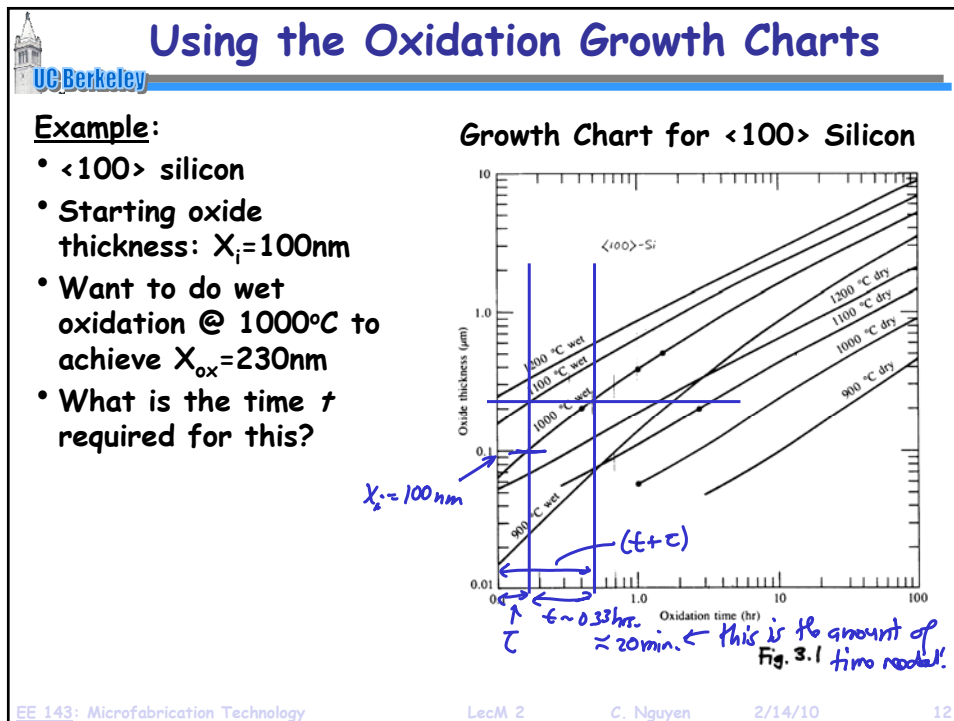
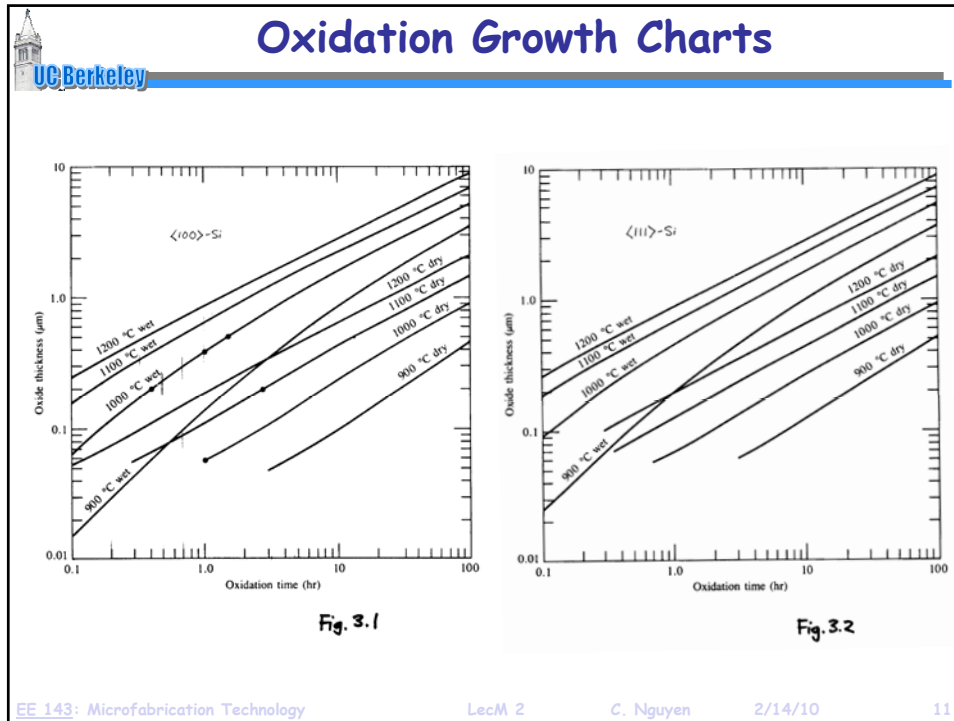
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Table 6-2 Rate constants describing (111) silicon oxidation kinetics at 1 Atm total pressure. For the corresponding values for (100) silicon, all C_2 values should be divided by 1.68.

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

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

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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 \Rightarrow faster oxidation, since water has a higher solubility (i.e., D) in SiO_2 than O_2
 5. Crystal orientation:
 - $\langle 111 \rangle \leftarrow$ faster, because there are more bonds available at the Si-surface
 - $\langle 100 \rangle \leftarrow$ fewer interface traps; smaller # of unsatisfied Si-bonds at the Si- SiO_2 interface


EE 143: Microfabrication Technology LecM 2 C. Nguyen 2/14/10 13



Factors Affecting Oxidation

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


EE 143: Microfabrication Technology LecM 2 C. Nguyen 2/14/10 14

 **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-SiO₂ 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 SiO₂)
 2. Segregation coefficient, m:

$$m = \frac{\text{impurity equil. conc. in Si}}{\text{impurity equil. conc. in SiO}_2}$$

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 **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 H₂ is present as a by-product.

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

EE 143: Microfabrication Technology LecM 2 C. Nguyen 2/14/10 16

