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CHE323/CHE384
Chemical Processes for Micro- and Nanofabrication
www.lithoguru.com/scientist/CHE323

Lecture 12
Thermal Oxidation, part 3

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Reading:
Chapter 4, *Fabrication Engineering at the Micro- and Nanoscale*, 4th edition, Campbell

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Deal-Grove Model

Rate equation:

$$\frac{dt_{ox}}{dt} = \frac{B}{2t_{ox} + A}$$

Gives:

$$t_{ox}^2 + At_{ox} = B(t + \tau)$$

gas | SiO_2 | Si

t_{ox}

C_g, C_s, C_0, C_i

Step 1: oxygen diffuses from the bulk (C_g) to the wafer surface (C_s)

Step 2: oxygen diffuses from the wafer surface (C_0) to the silicon interface (C_i)

Step 3: oxygen reacts with silicon at the interface

$$A = 2D\left(\frac{1}{h} + \frac{1}{k_s}\right) \qquad B = \frac{2DHP_g}{N_1} \qquad \tau = \frac{t_o^2 + At_o}{B}$$

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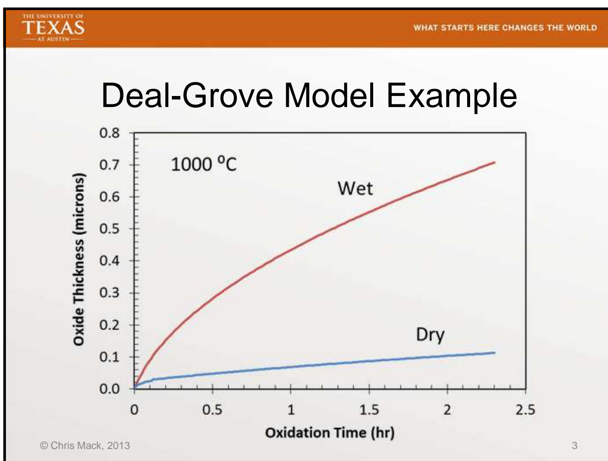
Deal-Grove Model Example



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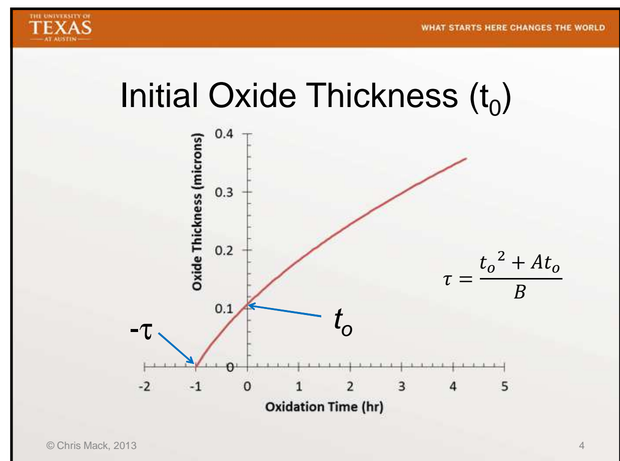
Initial Oxide Thickness (t_0)



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Deal-Grove Model Regimes

Rate equation: $\frac{dt_{ox}}{dt} = \frac{B}{2t_{ox} + A}$

Linear Regime:

For t_{ox} << A/2, $\frac{dt_{ox}}{dt} \approx \frac{B}{A}$ and $t_{ox} = \frac{B}{A}(t + \tau)$

Linear Rate Constant (B/A)

Parabolic Regime:

For t_{ox} >> A/2, $\frac{dt_{ox}}{dt} \approx \frac{B}{2t_{ox}}$ and $t_{ox}^2 = B(t + \tau)$

Parabolic Rate Constant (B)

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Model vs. Data

- When comparing model versus data, we find excellent agreement for wet oxidation
- For dry O_2 oxidation, the data shows a faster growth rate for the first 20 – 30 nm
  - The Deal-Grove model is not good at predicting oxide growth for thicknesses less than 30 nm
  - For thicker dry oxidation, we can use τ (or t_o) to account for the faster initial growth rate

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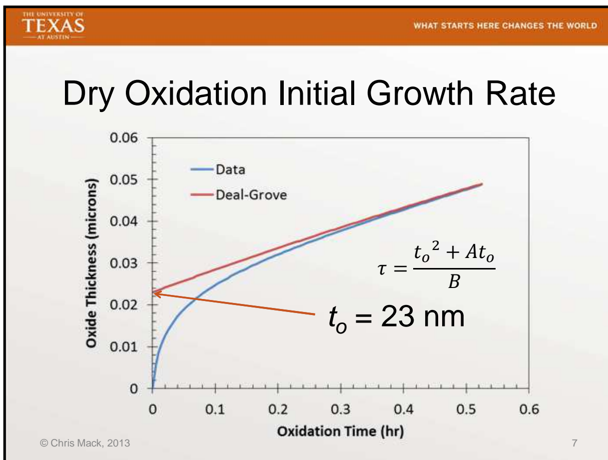
Dry Oxidation Initial Growth Rate



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Deal-Grove Parameters

TABLE 4.1 / OXIDATION COEFFICIENTS FOR SILICON (111) wafers

	Dry			Wet (640 torr)	
Temperature (°C)	A (μm)	B (μm²/hr)	τ (hr)	A (μm)	B (μm²/hr)
800	0.370	0.0011	9	—	—
920	0.235	0.0049	1.4	0.50	0.203
1000	0.165	0.0117	0.37	0.226	0.287
1100	0.090	0.027	0.076	0.11	0.510
1200	0.040	0.045	0.027	0.05	0.720

The τ parameter is used to compensate for the rapid growth regime for thin oxides *(after Deal and Grove)*.

(precision of constants is about ±2%)

Data From: B. E. Deal and A. S. Grove, "General Relationship for the Thermal Oxidation of Silicon", *Journal of Applied Physics*, **36**(12), 3770–3778 (Dec, 1965).

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Temperature Dependence

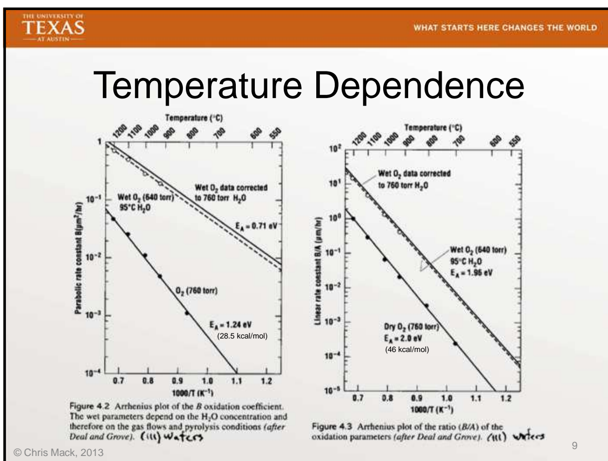

Figure 4.2 Arrhenius plot of the B oxidation coefficient. The wet parameters depend on the H_2O concentration and therefore on the gas flows and pyrolysis conditions *(after Deal and Grove)*. (111) wafers

Figure 4.3 Arrhenius plot of the ratio (B/A) of the oxidation parameters *(after Deal and Grove)*. (111) wafers

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Expected Parameter Behavior

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

$$B = \frac{2DHP_g}{N_1}$$ Temperature behavior determined by D

$$\frac{B}{A} \approx \frac{k_s HP_g}{N_1}$$ Temperature behavior determined by k_s

(Note: H is much higher for H_2O than for O_2)

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Pressure Dependence

- The model says A is independent of pressure, and B and B/A are proportional to partial pressure of oxidant
  - The is true experimentally for wet oxidation
  - For Dry O_2, we find that

$$\frac{B}{A} \propto P_g^{\,n}, \qquad 0.5 < n < 1$$

Why? If molecular oxygen diffuses and reacts, we would expect n = 0.5. If both O and O_2 are involved, 0.5 < n < 1.

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Crystal Orientation

- The number of silicon atoms per unit area on the wafer surface depends on the crystal orientation, but what matters is the number of Si-Si bonds per unit area
  - This affects k_s
  - (111) wafers have highest surface bond density
- The consequences:
  - B is independent of k_s and thus crystal orientation
  - For (100) wafers, B/A is 1.68X smaller (A is 1.68X higher) than for (111) wafers

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Other Factors

- Substrate Doping
  - Higher doping levels causes an increase in B/A (but not B)
  - This is probably due to an increase in crystal defects that allows for faster volume expansion
- Adding HCl to the gas
  - Recall that HCl is added (1-3%) to remove metal ions
  - This addition also causes an increase in oxidation rate (probably because HCl reacts with O_2 to form water)

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Oxide Growth Geometry

ρ_{Si} = 2.33 g/cm^3 ρ_{SiO2} = 2.27 g/cm^3

AW_{Si} = 28.09 g/mol MW_{SiO2} = 60.09 g/mol

$\textit{Molar Density}_{Si}$ = 0.0830 mol/cm^3

$\textit{Molar Density}_{SiO2}$ = 0.0378 mol/cm^3

$$\frac{\textit{Molar Density}_{SiO2}}{\textit{Molar Density}_{Si}} = 0.455 = \frac{\textit{Thickness of Si consumed}}{\textit{Thickness of } SiO_2 \textit{ grown}}$$

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Lecture 12: What have we learned?

- Be able to make calculations using the Deal-Grove model
- What are the linear and parabolic rate constants?
- Understand how to use τ when an initial oxide film is on the wafer
- Understand why τ is used for dry oxidation calculations for film thickness > 30 nm
- How does pressure affect oxidation rates?
- How does crystal orientation affect oxidation rates?

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