Lecture 12: Oxidation
Chapter 3 Jaeger

Last Time

• Before the break we covered the basics of diffusion.
Useful Links

This subject is widely taught, and online notes are available from many sources. Here are some good examples:

UC Berkeley Notes:
- [http://www-inst.eecs.berkeley.edu/~ee143/fa10/lectures/Lec_06.pdf](http://www-inst.eecs.berkeley.edu/~ee143/fa10/lectures/Lec_06.pdf)

UC Santa Barbara Notes:
- [https://engineering.ucsb.edu/~sumita/courses/Courses/ME141B/ME141B_lecture_4_F10.pdf](https://engineering.ucsb.edu/~sumita/courses/Courses/ME141B/ME141B_lecture_4_F10.pdf)

Lecture 11

- Oxide Properties.
- Oxidation Process.
- Oxide Growth Model.
- Factors Influencing Oxidation Rate.
Oxide Properties

Oxidation

- Reasons that SiO$_2$ so widespread in VLSI:
  - Forms directly from the Si substrate upon exposure to oxygen containing species (O$_2$ or H$_2$O):
    \[
    \text{Si(S)} + \text{O}_2(G) \rightarrow \text{SiO}_2(S) \quad \text{“Dry”}
    \]
    \[
    \text{Si(S)} + 2\text{H}_2\text{O(L)} \rightarrow \text{SiO}_2(S) + 2\text{H}_2(G) \quad \text{“Wet”}
    \]
  - SiO$_2$ is a high quality electrical insulator (low interface trap density):
    - Thin (10-50 Å) gate oxide for MOS gate.
    - Thick (1000-2000 Å) field oxide for transistor isolation and barrier to dopant diffusion.
Other Compounds

- This is one of the main advantages of Si, and is the main reason why it is the commercial standard for semiconductors.

### Germanium

![Graph of Germanium's Native Oxide Thickness vs Time](image)

**Hu et al.** “Native Oxidation Growth on Ge(111) and (100) Surfaces.” *Small* 4(6) (2008): 429.

### GaAs

![Graph of GaAs's J-V Characteristics](image)


Structure of SiO₂

- Each Si surrounded tetrahedrally by 4 O atoms
- Open, amorphous structure.

![Structure of SiO₂](image)

- Density of SiO₂ < crystalline SiO₂:
  - Quartz = 2.65 gm/cm³.
  - Thermally grown oxide = 2.20 gm/cm³.
  - Silicon = 2.33 gm/cm³.
Properties of SiO$_2$

- Excellent electrical insulator.
  - Resistivity $> 10^{15}$ Ωcm.
  - Band gap $\sim 8$ eV.
  - Crucial in devices.

Properties of SiO$_2$

- High breakdown electric field strength.
  - $>10$ MV/cm.
Properties of SiO$_2$

- Stable:
  - Down to $10^{-9}$ Torr, $T > 900^\circ C$.
  - Conformal oxide growth on exposed Si surface.

- Good diffusion mask for common dopants:
  \[ D_{SiO_2} \ll D_{Si} \]

- Excellent etch selectivity between Si and SiO$_2$. 

Oxidation: Applications

• Oxide grown by oxidation is used at two important steps in chip manufacture.
  • Field oxide.
  • Gate oxide.

• **Field oxide:**
  • Field oxide isolates different transistors on a chip.

![Field oxide diagram]

Oxidation: Applications

• **Gate oxide**
  • Recall that the gate on a transistor works because the charge effects the holes and electrons across the oxide

![Gate oxide diagram]

• Currently the gate oxide is only 10 - 50 Å thick. (A sheet of paper is 1,000,000 Å thick!)
Oxidation Techniques

- There are a few other ways to grow oxides:
  - Thermal oxidation (heated in oxygen-rich environment).
  - Chemical vapor deposition (CVD).
  - Plasma anodization.
  - Physical vapor deposition (PVD).

- Thermal oxidation is by far the prevalent in industry.
  - Best quality oxide.
  - Typically used for insulation.
  - Unfortunately requires high temperature.
  - We will focus on this technique.
Thermal Oxidation

- Two approaches:
- Dry Oxidation ($O_2$):
  - Uses oxygen gas: $Si(S) + O_2(G) \rightarrow SiO_2(S)$
  - High quality.
  - Slow oxidation rate.
  - Small maximum thickness (i.e. gate oxide).
- Wet Oxidation ($H_2O$):
  - Uses water vapor: $Si(S) + 2H_2O(Vapor) \rightarrow SiO_2(S) + 2H_2(G)$
  - Diffusion speed is higher.
  - Lower quality.
  - Faster oxidation rate.

Oxidation: Mechanism

- The oxygen containing species must diffuse through the oxide layer to the unreacted silicon.
- This makes for a “cleaner” process.
Oxidation: Mechanism

- Oxygen reacts with silicon to form silicon dioxide:
  \[
  \text{Si(S)} + \text{O}_2(G) \rightarrow \text{SiO}_2(S) \\
  \text{Si(S)} + 2\text{H}_2\text{O(Vapor)} \rightarrow \text{SiO}_2(S) + 2\text{H}_2(G)
  \]

- We can work out the thickness of Si consumed from the number density.

\[
X_{Si} = X_0 \frac{n_{ox}}{n_{Si}} \\
X_{Si} = X_0 \frac{2.3 \times 10^{22}}{5 \times 10^{22}} = 0.46X_0
\]

Oxide Growth Model
Deal & Grove Model

- Without easy growth of SiO$_2$ on Si, there would be no semiconductor industry.
- It’s no accident that the world leader in Si chip technology, Intel, has been led by Andy Grove.
- As a young researcher at Fairchild Semiconductor, he “wrote the book” on SiO$_2$ growth: the Deal-Grove model.

1997

Deal & Grove Model

- We will talk about dry growth (O$_2$), but principles are the same for H$_2$O.
- SiO$_2$ growth occurs at the Si/SiO$_2$ interface because:

\[
D^O_2(SiO_2) ≫ D^Si(SiO_2)
\]

I.e. diffusion coefficient of O$_2$ in SiO$_2$ is much higher than the diffusion coefficient of Si in SiO$_2$.

- We want to quantify the growth rate of the oxide.
- For this class we will carry out only parts of the derivation, and use the results. It closely follows the textbook.
  - A more in-depth derivation can be found in ECE611.
Modelling Oxidation

• The oxidation process is best visualized by this picture:

![Diagram of oxidation process](image)

• In order for oxidation to occur, oxygen must reach the silicon interface.
• As the oxide grows, the oxygen must pass through more SiO$_2$, and the growth rate will slow.
• The figure on the right is one way to visualize the process.

Oxidation Diagram

• The labels are as follows:
  • $N$ is the concentration of O$_2$ (# / volume).
  • $x$ is the distance from the surface of the oxide.
  • $X_0$ is the distance of the interface between the Si and SiO$_2$ from the surface (will change with time).
  • $N_i$ is the concentration of O$_2$ at the interface between the Si and SiO$_2$.
  • $J$ is the oxygen flux (# / area / time).
• We will assume the flux is the same at every position up to $X_0$. 
Modelling Oxidation

- We can describe the flux ($J$) using Fick’s First Law:
  \[
  J = -D \frac{\partial N(x,t)}{\partial x}
  \]  
  \[\text{(3.3)}\]

- Where $D$ is the diffusion coefficient of $O_2$ in $SiO_2$.
- The negative sign means that particles tend to move from regions of high concentration to regions of low concentration.
- For our derivation we are going to make the approximation that oxygen flux is constant everywhere and that $N \propto x$.
- In this case we can just approximate Fick’s First Law as:
  \[
  J = -D \frac{N_i - N_0}{X_0 - 0} = -D \frac{N_i - N_0}{X_0} \]  
  \[\text{(3.4)}\]

Oxidation Reaction

- We quantify the conversion of silicon and oxygen into $+ O_2$ to $SiO_2$ via a chemical reaction rate: $k_s$. This has units of length / time, (e.g. cm/s).
- At the interface between the $SiO_2$ and $Si$ we assume the oxidation rate ($k_s$) is proportional to the concentration of $O_2$ at the interface ($N_i$):
  \[
  J = k_s N_i
  \]  
  \[\text{(3.5)}\]
- Equating $N_i$’s in these two equations:
  \[
  J = \frac{DN_0}{(X_0 + D/k_s)}
  \]  
  \[\text{(3.6)}\]
Oxide Growth Rate

• So, by balancing diffusion with reaction rate we can describe the $O_2$ flux as:

$$J = \frac{DN_0}{(X_0 + D/k_s)}$$  \hspace{1cm} (3.6)

• Recall, our goal is to determine the rate of oxide growth:

$$\frac{dX_0}{dt}$$

• We define the number of oxygen molecules incorporated into a unit volume of the resulting oxide as $M$.
  • $M$ is a number density and has dimensions of #/[length]$^3$.
  • We can hence infer through dimensional analysis:

$$\frac{dX_0}{dt} = J/M = \frac{DN_0}{M(X_0 + D/k_s)}$$  \hspace{1cm} (3.7)

• We identify this a first order ordinary differential equation.
  • We are not going to solve it, we will just take the solution:

$$X_0(t) = 0.5A \left[ 1 + \frac{4B}{A^2} (t + \tau) \right]^{1/2} - 1$$  \hspace{1cm} (3.9)

• Where:
  $$A = \frac{2D}{k_s} \quad B = \frac{2DN_0}{M}$$
  • Bare silicon is very reactive, and in air you will always find your wafer has some native oxide (even if it is only ~10Å).
  • And $\tau$ is the time it would have taken to grow the initial oxide.

• You can think of $\tau$ as the time before $t = 0$ required to grow this native oxide.
Oxide Thickness

\[ X_0(t) = 0.5A \left[ 1 + \frac{4B}{A^2} (t + \tau) \right]^{1/2} - 1 \]  

(3.9)

- This is the equation that tells us how thick our oxide would be for a certain oxidation time \( t \) and certain parameters \( (A, B, \tau) \).
- Growth parameters are often quoted with this notation:
  - Be aware of the non-standard units for length and time.

Growth Regimes

\[ X_0(t) = 0.5A \left[ 1 + \frac{4B}{A^2} (t + \tau) \right]^{1/2} - 1 \]  

(3.9)

- It turns out we can simplify this equation for different times.
- We define **Short Times** as \( t + \tau \ll A^2/4B \):
  
  \[ X_0(t) = \frac{B}{A} (t + \tau) \]  

(3.10)

- We define **Long Times** as \( t + \tau \gg A^2/4B, t \gg \tau \):
  
  \[ X_0(t) = \sqrt{Bt} \]  

(3.11)

- For this reason, sometimes \( A/B \) is the called the **Linear Coefficient** and \( B \) is called the **Parabolic Coefficient**.
Growth Regimes

- If we plotted the oxide thickness ($X_0$) as a function of growth time, we would hence expect to observe something like this:

Factors Influencing Oxidation Rate
Diffusion Coefficient

- As we talked about in the last lecture, diffusion is a temperature-activated process:
  \[ D = D_0 \exp \left( \frac{-E_A}{k_B T} \right) \]  
  (3.12)

- Where:
  - \( D \) is the diffusion coefficient (of oxygen in SiO\(_2\)).
  - \( D_0 \) is the diffusion pre-factor.
  - \( E_A \) is the activation energy.
  - \( k_B \) is the Boltzmann Constant.
  - \( T \) is the Temperature.

Diffusion Coefficient

<table>
<thead>
<tr>
<th>Wet O(_2)(X(_i) = 0 nm)</th>
<th>Dry O(_2)(X(_i) = 25 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_0 )</td>
<td>( E_A )</td>
</tr>
<tr>
<td>Linear (B/A)</td>
<td>9.70 \times 10^3 \mu m/hr</td>
</tr>
<tr>
<td>Parabolic (B)</td>
<td>388 \mu m(^2)/hr</td>
</tr>
<tr>
<td>Linear (B/A)</td>
<td>1.63 \times 10^3 \mu m/hr</td>
</tr>
<tr>
<td>Parabolic (B)</td>
<td>388 \mu m(^2)/hr</td>
</tr>
</tbody>
</table>

- \( \)<100\> Silicon
- \( \)<111\> Silicon

- Dry oxide:
  - 700-1,200 °C.
  - 1 atm (101325 Pa).
  - Typical = 100nm/hr.
  - SiO\(_2\) Density is higher.
  - Used for gate oxide.

- Wet oxide:
  - 750-1,100 °C.
  - 25 atm (2.5 \times 10^6 Pa).
  - Typical = 1\mu m/hr.
  - SiO\(_2\) Density is lower, more porous.
  - Used for field oxide and etch oxide.
Growth Rate Constants

\[ A = \frac{2D}{k_S} \]

\[ B = \frac{2DN_0}{M} \]

- The rate constants / coefficients are also \( T \)-dependent.

**Figure 3.4**
Dependence of the parabolic rate constant \( B \) on temperature for the thermal oxidation of silicon in pyrogenic \( \text{H}_2\text{O} \) (640 torr) or dry \( \text{O}_2 \). Reprinted by permission of the publisher, The Electrochemical Society, Inc., from Ref. [10].

**Figure 3.5**
Dependence of the linear rate constant \( B/A \) on temperature for the thermal oxidation of silicon in pyrogenic \( \text{H}_2\text{O} \) (640 torr) or dry \( \text{O}_2 \). Reprinted by permission of the publisher, The Electrochemical Society, Inc., from Ref. [10].
First Substrates are Cleaned

- RCA Clean (Lecture 2)
  - Organic strip.
    - Piranha Solution.
  - Native oxide removal.
    - HF.
  - Heavy metal removal.
    - HCl:H₂O₂:H₂O.
  - Dump rinse.
    - 18 MΩcm DI H₂O.
  - Spin Dry.

Initial Oxidation Regime

- Experimentally, this is observed:

![Graph showing oxidation rate vs. oxide thickness]
**Initial Oxidation Regime**

- Many models have been proposed.
- It is likely the $\text{O}_2$-$\text{SiO}_2$ interface is not abrupt:

![Initial Oxidation Regime Diagram]

**Dopants**

- Common dopants in Si enhance oxidation at higher concentration

**Boron**

Oxide thickness vs. wet oxidation time at 640 mTorr for three different boron concentrations (Sze)

**Phosphorus**

Data for dry oxidation at 1 atm and 900°C

Linear, $B/A$, and parabolic, $B$, rate constants vs. phosphorus concentration.
**Oxidation Reactor**

- Oxidation is carried out in a horizontal or vertical reactor.
- Many wafers are held in a vertical holder and pure water is pumped through.

![Oxidation Reactor Diagram](image)

- Pressure = 760 Torr (typical)
  - High concentration to help diffusion.
- Temperature = 900 ± 1 °C (typical)
  - High temperature to help diffusion.

**Equipment**

- You will become familiar with this equipment during lab sessions.
Summary

- We will have covered the growth of silicon oxide.

Next Time...

- Next time will start to cover transistors.