Lecture 4: Silicon Wafer Growth

Announcements

Homework 1/2:

- Will be online after the Lecture on Wednesday 10\textsuperscript{th} April.
- Total of 25 marks.
- Each homework contributes an equal weight.
  - All homework contributes to 20\% of overall grade.
  - Each homework contributes 10\% of overall grade.
- Due Wednesday 17\textsuperscript{th} April at the start of the lecture (4:00pm).
- I will return it one week later (24\textsuperscript{th} April).
- I will post the solutions when I return the homeworks.
- Homework 1 will consist of content covered in Lectures 1 - 6.
Last Time...

• We looked at the Basic properties of silicon.

https://youtu.be/ApqFLVd0XaI?t=9m10s

Lecture 4

• Requirements for Integrated Circuits.
• Sand to Electronic Grade Polysilicon.
• Polycrystalline to Single Crystal Silicon.
• Single Crystal Ingot to Wafer.
Requirements for Integrated Circuits

Impurity States

- Before we talk about the requirements of our wafers, let's talk about what impurities in silicon do.
- Depending on the impurity, we could end up creating additional states in our band gap.
Density of States
• If you plot the Density of States (DOS) vs Energy:

\[ \text{Density of States (cm}^{-3} \text{eV}^{-1}) \]

\[ \text{Energy (} E_s - E_F \text{) (eV)} \]

- Donor-like States
- Band States
- Acceptor-like States
- Tail States
- Deep States
- Dangling Bonds


Trap States
• So these trap states can potentially act as traps to both holes and electrons.
• They significantly hinder the ability of charge carriers to be transported over long distances.
**Target Properties of Si Wafers**

- We will just quote the requirements of our wafers:
- Extremely pure feed: 99.9999999% (9 nines).
  - Oxygen and carbon are carefully controlled.
  - Some oxygen is beneficial.
- Very flat: 775µm ± 10µm over 300 mm.
- Precise diameter: 300 mm ± 0.2 mm.
- Precise resistivity and doping.
- Crystalline orientation <111> or <100>.
  - Important for doping and for die separation.
- Very low crystalline defects.
- Very low numbers of surface particles (ppm).

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**Sand to Electronic Grade Polysilicon (EGS)**
Sand to EGS

- The first stage in forming wafer is to convert sand (SiO$_2$) into Electronic Grade (polycrystalline) Silicon - EGS.
- The next process step (Czochralski growth) adds impurities into the material, so EGS needs to be very pure to begin with.
- EGS is an incredibly pure form of polycrystalline silicon.
  - 99.9999999% (9 nines) pure.
  - Or, impurity levels of parts per billion (ppb). Equivalently $10^{13}$ cm$^{-3}$.
- The starting materials is often quartzite - a relatively pure form of SiO$_2$.

Sand to EGS

Overall Process Flow:

- Essentially what we want to achieve is:
  $$\text{SiO}_2 \rightarrow \text{Si} + \text{O}_2$$
Sand to EGS

Step 1:
- The first step is to reduce SiO$_2$ to MGS.
- MGS is Metallurgical Grade Silicon.
- As the name suggests, it is an appropriate grade for metallurgical applications.
- Often used in small parts in the automotive industry.
- Normally as an alloy with another metal (e.g. aluminum).

<table>
<thead>
<tr>
<th>Typical Impurities in MGS</th>
<th>Element</th>
<th>Conc. (ppm)</th>
<th>Element</th>
<th>Conc. (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>1000-5000</td>
<td>B</td>
<td>35-50</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>20-50</td>
<td>Ca</td>
<td>250-600</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>50-200</td>
<td>Cu</td>
<td>15-60</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>1600-6500</td>
<td>Mn</td>
<td>50-100</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>2-20</td>
<td>Ni</td>
<td>20-100</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>150-300</td>
<td>V</td>
<td>50-250</td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>20-30</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Sand to EGS

Step 1:
- A mixture of wood chips, coal and coke supply carbon.
- The reaction then takes place as follows:

\[
\text{SiO}_2(S) + 2C(S) \rightarrow \text{Si}(L) + 2\text{CO}(G)
\]

- Liquid silicon is extracted from the bottom.
- At this stage it is roughly 98% pure.
Sand to EGS

Step 2:

- The next step is to convert the MGS into SiHCl\(_3\) (trichlorosilane).

  - SiHCl\(_3\) is liquid at room temperature.
  - Melting point = -127°C.
  - Boiling point = +32°C.

- The MGS is converted to a powder so that it can be used in a fluidized bed.

![Fluidized Bed Diagram](https://www.youtube.com/watch?v=FcNuxk8vDu8)
Sand to EGS

Step 3:
- The SiHCl₃ (trichlorosilane) obtained in Step 2 contains impurities:
  - Boron Trichloride (BCl₃).
  - Phosphorous Trichloride (PCl₃).
- Because trichlorosilane has a boiling point of 32°C it can be purified using distillation.
  - 6-8 trays are used.
- We are still left with SiHCl₃, which is neither silicon, nor a solid at room temperature.

Sand to EGS

Step 4:
- The SiHCl₃ is used as the precursor gas in CVD deposition.
- CVD = chemical vapor deposition.
  \[ \text{SiHCl}_3(G) + 2\text{H}_2(G) \rightarrow 2\text{Si}(S) + 6\text{HCl}(G) \]
- Deposition temperature is 950°C to 1100°C.
- Called the Siemens Process.
- The final product is EGS: 99.9999999% (9 nines) pure.
Solar Grade Silicon

- The process we have described so far yields Electronic Grade Silicon (polycrystalline).
- For certain applications, this level of purity is not necessary.

- $5N = 99.99\%$
- $9N = 99.9999\%$

Polycrystalline to Single Crystal Silicon
Polycrystalline Silicon

- So far we have produced very pure, but polycrystalline, silicon.
- What do we mean by polycrystalline silicon (poly-Si)?
- A polycrystalline system possesses local order, but over long-distances exhibits some disorder:

Polycrystalline Materials

- Basically we have many regions of fully ordered crystalline silicon.
- However these regions all have different crystallographic orientations separated by grain boundaries.
- It turns out grain boundaries a big problem.
Polycrystalline Silicon

- This is a top-down SEM Image of a poly-Si film:

Non-Uniformity

- By its nature, polycrystalline silicon is very inhomogeneous.
- Device-to-device variation is very large indeed.
- In particular channel length-dependence.
Single Crystal Silicon

- Especially down at the nanometer scale, we cannot afford to have significant device-to-device variation.
- To make microelectronics viable, we therefore require single-crystal silicon.

- The next stage of the process involves converting polycrystalline silicon to single-crystal silicon.

Czochralski (CZ) Growth

- The most common technique used to form single crystal ingots of silicon is the Czochralski Method.
- Named after Jan Czochralski (Polish Chemist).
- Developed in the 1950s, and is still the dominant method for crystal growth.
Czochralski (CZ) Growth

- The process (briefly) is as follows:
  - Crucible loaded with electronic grade silicon (EGS).
  - Chamber pumped down, and filled with inert gas (e.g. Argon).
  - Charge is melted (melting point of silicon is 1421°C).
  - A seed crystal (5mm diameter, 100-300mm long) is lowered into melt.
  - It is withdrawn at a controlled rate to form crystal ingot.

Modeling of CZ

- Modelling of the Czochralski process can be incredibly complex.

- We will restrict our considerations to:
  - Maximum growth velocity of the Si Boule.
  - Impurity concentrations along the Boule.

Inputs
- Geometry
- Properties
- Initial Conditions

Governed Equations:
- Mass
- Momentum
- Energy (Charge)

Outputs
- Growth velocity
- Concentrations
- Diameter
Si/Impurity Phase Diagram

- We can visualize the phases of the material with a phase-diagram.

![Phase Diagram](image)

Segregation Coefficient

- We operate in the regime of very low impurity concentrations:

![Segregation Coefficient](image)

- The ratio of these two concentrations is defined as the Segregation Coefficient ($k_0$):

$$k_0 = \frac{C_i^S}{C_i^L}$$
Segregation Coefficient

- What does $k_0$ tell us?

$$k_0 = \frac{C_i^s}{C_i^l}$$

- If $k_0 < 1$ ($C_i^s < C_i^l$):
  - The Liquidus is above Solidus (as shown).
  - Impurities tend to segregate into liquid.
- If $k_0 > 1$ ($C_i^s > C_i^l$):
  - The Solidus is above Liquidus (opposite to what is shown).
  - Impurities are tend to segregate into the solid.

Values of $k_0$

- Values for common dopants and impurities with respect to silicon:

<table>
<thead>
<tr>
<th>Element</th>
<th>$k_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0.8</td>
</tr>
<tr>
<td>P</td>
<td>0.35</td>
</tr>
<tr>
<td>Ga</td>
<td>$8 \times 10^{-3}$</td>
</tr>
<tr>
<td>As</td>
<td>0.3</td>
</tr>
<tr>
<td>Sb</td>
<td>0.023</td>
</tr>
<tr>
<td>O</td>
<td>1.4</td>
</tr>
<tr>
<td>Al</td>
<td>$2 \times 10^{-3}$</td>
</tr>
<tr>
<td>C</td>
<td>0.06</td>
</tr>
</tbody>
</table>

- Boron and Phosphorus could be put in intentionally.
- We see that elements tend to segregate to the liquid (except oxygen).
- Pulled crystals typically contain dopants, $\sim 10^{18}$ cm$^{-3}$ oxygen and $\sim 10^{16}$ cm$^{-3}$ carbon.
Normal Freezing Relation

- With knowledge of $k_0$, we can quantify the expected concentration of impurities in the pulled ingot, in terms of the concentration of impurities in the melt.
- We do this via the Normal Freezing Relation:

$$C_S = k_0 C_0 (1 - X)^{k_0 - 1}$$

- Where:
  - $X$ is the fraction of the melt solidified.
  - $C_0$ is the initial melt impurity concentration.
  - $C_S$ is the solid impurity concentration.
  - $k_0$ is the segregation coefficient.

Example

- We seek to grow an Si ingot using the CZ process, with a boron (B) impurity concentration of $10^{15}$ atoms / cm$^3$, halfway through the process.
  - For 60kg of Si charge, how many grams of B are required?

- For boron:
  - $k_0 = 0.8$.
  - Atomic weight = 10.8 g/mol.
  - Density of liquid Si = 2.53g / cm$^3$.

$$C_S = k_0 C_0 (1 - X)^{k_0 - 1}$$

- We seek $C_0$:

$$C_0 = \frac{C_S}{k_0 (1 - X)^{k_0 - 1}}$$
Example

- Halfway through the process $X \approx 0.5$.
  
  $$C_0 = \frac{C_S}{k_0(1 - X)^{k_0-1}}$$

- Put in values (work in cm$^{-3}$):
  
  $$C_0 = \frac{10^{15}}{0.8 \times (1 - 0.5)^{0.8-1}} = 1.1 \times 10^{15} \text{ cm}^{-3}$$

- Next determine volume of molten silicon:
  
  $$V = \frac{m}{\rho} = \frac{60 \times 10^3 \text{ g}}{2.53 \text{ g/cm}^3} = 2.37 \times 10^4 \text{ cm}^3$$

- Number of B atoms in the melt:
  
  $$N_B = VC_0 = 2.37 \times 10^4 \text{ cm}^3 \times 1.09 \times 10^{15} \text{ cm}^{-3} = 2.58 \times 10^{19}$$

Example

- Number of B atoms in the melt:
  
  $$N_B = 2.58 \times 10^{19}$$

- Determine mass of boron atoms:
  
  - Use Avagadro’s number $N_A = 6.023 \times 10^{23} \text{ atoms / mol}$:
    
    $$m = \frac{N_B u}{N_A} = \frac{2.58 \times 10^{19} \times 10.8}{6.023 \times 10^{23}} = 4.62 \times 10^{-4} \text{ g}$$

  - 10.8 g/mol
From Boule to Wafer

- We are not going to go into depth on how to cut wafers.
- (It is done with a saw.)
From Boule to wafer

After Wafer Sawing
- Diameter: 10mm, Thickness: 76 µm

After Wafer Sawing
- Diameter: 200mm, Thickness: 12.5 µm

After Lapping
- Diameter: 300mm, Thickness: <2.5 µm

After Etch
- Diameter: 450mm, Thickness: 2.5 µm

After CMP
- Diameter: Virtually Defect Free, Thickness: 725 µm

Wafer Dimensions

<table>
<thead>
<tr>
<th>Diameter (mm)</th>
<th>Thickness (µm)</th>
<th>Area (cm²)</th>
<th>Weight (grams)</th>
<th>Weight/25 Wafers (lbs)</th>
<th>10mm Die/Wafer</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>675 ± 20</td>
<td>176.71</td>
<td>28</td>
<td>1.5</td>
<td>143</td>
</tr>
<tr>
<td>200</td>
<td>725 ± 20</td>
<td>314.16</td>
<td>53.08</td>
<td>3</td>
<td>269</td>
</tr>
<tr>
<td>300</td>
<td>775 ± 20</td>
<td>706.86</td>
<td>127.64</td>
<td>7</td>
<td>640</td>
</tr>
<tr>
<td>450</td>
<td>925 ± 20</td>
<td>1590.43</td>
<td>342.78</td>
<td>19</td>
<td>1490</td>
</tr>
</tbody>
</table>

\[ DPW = d \pi \left( \frac{d}{4S} - \frac{1}{\sqrt{2S}} \right) \]

Dies per wafer
- \( d \) = wafer diameter (mm)
- \( S \) = die size (mm²)
Summary

- We have covered the basics of how we can grow single crystal wafers of silicon from SiO$_2$ precursor materials.

Next Time...

- We will look at the operation of metal-oxide-semiconductor (MOS) capacitors.

$$V(x) = V(x_0)$$

$V_{in}$

$V_{err}$

+Q

-Q

Metal

Oxide

Semiconductor

Metal