Semiconductor Processing: Crystal Growth

Professor Benjamín Alemán
Department of Physics
University of Oregon
How do we make these useful and curious structures?
Planar Processing with Semiconductors (Silicon): Course Map

- Crystal growth (semiconductors)
- Wafer characteristics
- Wafer doping
- Defects and impurities
- (SiO₂ growth)

- (SiO₂ growth)
- Masked doping
- Lithography
- Vacuum Systems
- Thin Films: CVD, MBE, PVD, ALD
- Implantation
- Wet and Dry Etching
- Integration
Why are semiconductors useful?

Types of Semiconductors:
- Si: Elemental
- GaAs: III-V Binary Compound
- ZnSe, CdTe: II-VI Binary Compound
- Organic
Why is Silicon an important semiconductor and why is it so popular in planar processing?

- 26% by mass of Earth’s crust
- Over 90% of Earth’s crust is silicate materials.
Silicon is abundant

*from P.H. Stauffer et al, Rare Earth Elements - Critical Resources for High Technology, USGS (2002)*
A brief introduction to crystal structure

Crystal Structure = Lattice + Basis

A lattice is defined by a set of fundamental translation vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$, such that the atomic arrangement looks the same from the perspective of both $\mathbf{r}$ and $\mathbf{r}'$, where

$$\mathbf{r}' = \mathbf{r} + u_1 \mathbf{a}_1 + u_2 \mathbf{a}_2 + u_3 \mathbf{a}_3$$

and $u_1, u_2, u_3$ are arbitrary integers.
The basis
Cubic lattices

Salt is FCC with basis containing one Na and one Cl.

Diamond is FCC with two identical basis atoms:

All group IV elements can crystallize into diamond, including C and Si.
Index system for crystal planes

Crystal planes are identified using Miller indices in the following way:

1. Find the intersection of the axes in terms the basis of the fundamental translation vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$.
2. Take the reciprocal and reduce to three integers having the same ratio, usually the smallest three integers. The result is enclosed in parentheses $(hkl)$ and called the index of the plane. Negative integers are denoted with bars $(\bar{h}\bar{k}\bar{l})$.

Also, planes equivalent by symmetry are denoted with braces $\{hkl\}$.

- The set of cube faces is $\{100\}$.

The indices $[uvw]$ of a direction in a crystal are the set of the smallest integers that have the ratio of the components of a vector in the desired direction.

- The $\mathbf{a}_1$ axis is the $[100]$ direction, the $-\mathbf{a}_2$ axis is the $[0\bar{1}0]$ direction.

- **NB**: In cubic crystals, the direction $[hkl]$ is perpendicular to the plane $(hkl)$ having the same indices.
Index system for crystal planes

Plane intercepts the vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ axes at $3\mathbf{a}_1, 2\mathbf{a}_2, 2\mathbf{a}_3$. Reciprocals of these numbers are $\frac{1}{3}, \frac{1}{2}, \frac{1}{2}$. Small integers having the same ratio are 2, 3, 3, thus indices of the plane are (233).
Examples of indexed crystal planes

Si (100)

Si (111)
## Crystal Growth: Silicon and Gallium Arsenide

<table>
<thead>
<tr>
<th>Advantages of Si</th>
<th>Advantages of GaAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Cheaper</td>
<td>• Higher electron mobility</td>
</tr>
<tr>
<td>• More stable and less defects, better for VLSI</td>
<td>• Higher saturation velocity</td>
</tr>
<tr>
<td>• Bigger wafers</td>
<td>• Good for MW electronics (250GHz)</td>
</tr>
<tr>
<td>• SiO₂</td>
<td>• Direct Band Gap: emits and absorbs efficiently; for LEDs, Lasers, and PVs</td>
</tr>
<tr>
<td>• Pure element, easier to make</td>
<td>• Can make AlₓGa₁₋ₓAs which allow HEMTs.</td>
</tr>
<tr>
<td>• Higher hole mobility (for CMOS)</td>
<td></td>
</tr>
</tbody>
</table>

- How we make single-crystal Si and GaAs?
- How we shape into wafers?
- Characteristics of wafers?
Manufacture of single-crystal Silicon requires high purity raw Silicon, made by the *Siemens Process*

Quartzite + Carbon

\[
\text{SiC (solid) + SiO}_2\text{(solid)} \rightarrow \text{Si (solid) + SiO (gas) + CO (gas)}
\]

98% pure MGS, which is then pulverized

\[
\text{Si (solid) + 3HCl (gas)} \xrightarrow{300^\circ C} \text{SiHCl}_3\text{(gas) + H}_2\text{ (gas)}
\]

Forms trichlorsilane (boils at 32 C), which is then distilled for hydrogen reduction

\[
\text{SiHCl}_3\text{(gas) + H}_2\text{(gas)} \rightarrow \text{Si (solid) + 3HCl (gas)}
\]

Produces very pure polycrystalline EGS on a heated Si rod in chamber. Impurity range is in parts-per-billion (ppb).
The Czochralski (CZ) technique: the crystal puller
The CZ technique in pictures

1412° C

Dopants (e.g. B)

[111] or [100]

Molten Si freezes onto Si seed.

Si ingots are 200 kg in mass and 300 mm in diameter
Wafer size projections

The bigger, the cheaper?
How is do we dope Silicon?

- Melting of polysilicon, doping
- Crystal pulling
Doping profiles of Silicon ingots

The concentration of dopant in liquid and solid phases of Si is not the same and changes during growth.

The *equilibrium segregation coefficient*:

\[ k_0 = \frac{C_s}{C_l} \]

Equilibrium concentrations

<table>
<thead>
<tr>
<th>Dopant</th>
<th>( k_0 )</th>
<th>Type</th>
<th>Dopant</th>
<th>( k_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>( 8 \times 10^{-4} )</td>
<td>( p )</td>
<td>As</td>
<td>( 3.0 \times 10^{-4} )</td>
</tr>
<tr>
<td>Al</td>
<td>( 2 \times 10^{-3} )</td>
<td>( p )</td>
<td>Sb</td>
<td>( 2.3 \times 10^{-4} )</td>
</tr>
<tr>
<td>Ga</td>
<td>( 8 \times 10^{-3} )</td>
<td>( p )</td>
<td>Te</td>
<td>( 2.0 \times 10^{-3} )</td>
</tr>
<tr>
<td>In</td>
<td>( 4 \times 10^{-4} )</td>
<td>( p )</td>
<td>Li</td>
<td>( 1.0 \times 10^{-2} )</td>
</tr>
<tr>
<td>O</td>
<td>1.25</td>
<td>( n )</td>
<td>Cu</td>
<td>( 4.0 \times 10^{-3} )</td>
</tr>
<tr>
<td>C</td>
<td>( 7 \times 10^{-3} )</td>
<td>( n )</td>
<td>Au</td>
<td>( 2.5 \times 10^{-5} )</td>
</tr>
<tr>
<td>P</td>
<td>0.35</td>
<td>( n )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( k_0 < 1 \) means dopants are rejected by solid Si into the melt, so concentration in melt increases during growth. Also, if \( C_l \) increase, then \( C_s \) will too.
How does an increasing/decreasing dopant concentration in the liquid ($C_l$) affect the dopant concentration ($C_S$) in a growing Si crystal?
Doping distribution of Silicon ingots during growth

\[ C_s = k_0 C_0 \left( 1 - \frac{M}{M_0} \right)^{k_0 - 1}. \]

- Example

![Graph showing the doping distribution of Silicon ingots during growth](image-url)
Effective Segregation Coefficient

During crystal growth, the dopant can accumulate near the liquid-solid interface and cause a dopant concentration gradient ($k_0 < 1$):
How can we model the system to account for the stagnant layer?

Mass transport by diffusion and drift