Crystal Growth

1. Czochralski Technique (CZ)
2. Float-Zone Technique (FZ)

i. CZ:
- Most IC industries use CZ grown Crystal

Advantages:
- Large Diameter wafers
- Simpler Process and easy to control
  Impurity Conc.

Disadvantage:
- Contains many small amount of Impurities like Carbon, Oxygen, Iron etc.
ii) Float-Zone Technique

a) Costlier

b) Large size wafers cannot be grown.

c) However, it will have a very high degree of uniformity of impurities of choice (Dopants).

d) Highly pure silicon wafers with impurities like O, C, & Fe etc. are absent.

e) Resistivities of the order of 10000 ohm-cm and even 20000 ohm-cm are possible. Compared to CZ crystals which can have high 100 ~200 ohm-cm resistivity.
1. Doping - P or n type

2. Crystal Orientation < 100 >

3. Resistivity 0.1 ohm cm $\rightarrow$ 0.1 to 0.2 ohm cm

4. Dislocation Count: no $\uparrow$ dislocations/cm$^2$ EDP

5. Radial resistivity variation.

6. & Thickness

7. Diameter $\pm$ AD
Modeling Dopant Behaviour During Crystal Growth - Mathematical Representation

1. Dopants are added to the Melt to provide controlled n or p doping conc. in the wafers.

2. As said earlier, the problem of modeling becomes difficult because of impurity segregation in melt and solid.

Segregation Coeff.: \( k_0 = \frac{C_S}{C_L} = \frac{\text{Conc. of Solute (By wt.) in Solid}}{\text{Conc. of Solute (By wt.) in Liquid}} \)
Crystals are pulled from the melt with certain pull-rate and with spin rate of rotating crystal.

The impurities are added to the melt by weight and during solidification gets into lattice to form n or p Silicon.

Typical Dopants are

P-type: Boron, Aluminum, Gallium, Indium

N-type: Phosphorous, Arsenic (As), Antimony

Other Impurities: Oxygen, Carbon, Bi, Li, and Au
<table>
<thead>
<tr>
<th>Dopant/Impurity</th>
<th>Segregation Coeff. $K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0.8</td>
</tr>
<tr>
<td>Al</td>
<td>$2.8 \times 10^{-3}$</td>
</tr>
<tr>
<td>Ga</td>
<td>$8 \times 10^{-3}$</td>
</tr>
<tr>
<td>In</td>
<td>$3.6 \times 10^{-4}$</td>
</tr>
<tr>
<td>P</td>
<td>0.35</td>
</tr>
<tr>
<td>As</td>
<td>0.30</td>
</tr>
<tr>
<td>Sb</td>
<td>0.023</td>
</tr>
<tr>
<td>O</td>
<td>0.5</td>
</tr>
<tr>
<td>C</td>
<td>0.07</td>
</tr>
<tr>
<td>Li</td>
<td>$10^{-2}$</td>
</tr>
<tr>
<td>Bi</td>
<td>$7 \times 10^{-4}$</td>
</tr>
<tr>
<td>Au</td>
<td>$2.5 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
If $C_s = \text{Conc. of Impurities in Solid surface (By wt.)}$

& $C_L = \text{Conc. of Impurities in Liquid (Melt) (By wt.)}$

One defines segregation coefficient $k_0$ as

$$k_0 = \frac{C_s}{C_L}$$

Rapid Stirring Case:

Let $W_M = \text{Initial Weight of Melt}$

$C_M = \text{Conc. of Solute in Melt (By wt.)}$

During Crystal Growth, at any instant

$C_L = \text{conc. of Solute in Liquid}$

$C_s = \text{conc. of Solute in Solid}$
One defines $S$ as weight of solute in melt

\[
\begin{align*}
\text{Solid} & \quad \text{Consider } \, dw \, \text{is wt. of an element of a crystal of thickness } dr \, \text{in liquid} \rightarrow \frac{\text{dr}}{\text{dw}} \\
\therefore \text{Weight of solute lost from melt } S = ds \\
\therefore \quad ds = -C_s \, dw
\end{align*}
\]

At this instant of time

\[
\text{Wt. of Melt} = W_M - W
\]

\[
\therefore \text{Conc. } C_L = \frac{S}{W_M - W}
\]

As $k_0 = \frac{C_s}{C_L}$, we have

\[
\begin{align*}
\text{d}S &= -C_s \, dw \\
\end{align*}
\]

Please note that at initial time

\[
\begin{align*}
C_M &= \text{Conc. of solute in Melt} \\
W_M &= \text{Weight of Melt} \\
\therefore \text{Weight of solute at } t=0 \\
S_0 &= C_M \cdot W_M
\end{align*}
\]
\[
\therefore \, ds = -k_0 c_L \, dw \\
= -k_0 \, \frac{s}{w_{M-W}} \, dw \\
\Rightarrow \, \frac{ds}{s} = -k_0 \, \frac{dw}{w_{M-W}} \\
\therefore \, \int_{s_0}^{s} \frac{ds}{s} = -k_0 \, \int_{0}^{w} \frac{dw}{w_{M-W}} \\
\]

\[
s_0 = w_M c_M \\
\therefore \, c_s = k_0 c_M \left(1 - \frac{w}{w_M}\right)^{k_0-1}
\]

![Graph showing the relationship between \(C_s\) and \(C_M\) with \(k_0\) values](image)
Partial - Stirring Cond's

Slow Stirring creates a Stagnant Layer of thickness $\delta$ between Solid & Liquid.

The dopant diffuses through the Stagnant Layer ($\delta$) from Liquid into Solid.

Solving diffusion equation it can be shown that effective Segregation Coeff - $k_e$ is larger than $k_0$. 
If we pull the crystal, Solid-Liquid Interface also is pulled up by same pull rate.

If \( R \) = Growth Rate of Crystal

\( \Delta D = \) Diffusion Coefficient of Solute atoms in the Liquid (Top portion of Melt)

Typically \( D = 5 \times 10^{-5} \) cm²/sec for most impurities

Since impurities diffuse through the Stagnant Layer giving flux to Solid region. However during segregation process, solute is also rejected back to Liquid.

In equilibrium we can write

\[
D \frac{d^2C}{dx^2} + R \frac{dC}{dx} = 0
\]

Forward Reverse
Solution of Diff. Eq is

\[ C = A e^{-R x/D} + B \]

\[ \therefore \frac{dc}{dx} = -\frac{AR}{D} e^{\frac{-R x}{D}} \]

Boundary condns: (i) \( C = C_L' \) at \( x = 0 \)

(ii) \( \left. \frac{dc}{dx} \right|_{x=0} = -\frac{R}{D} (C_L' - C_s) \)

The equivalent Keff \( Ke = \frac{C_s}{C_L} \) & \( k_0 = \frac{C_s}{C_L'} \)
It is found that \( ke = \frac{Cs}{C_L} \) which is now

\[
ke = \frac{k_0}{k_0 + (1-k_0)e^{-D}} \quad \text{Here } k_0 = \frac{Cs}{C_L'}
\]

where \( R = \text{Rate of growth of Crystal} \)
\( D = \text{Diffusion Coeff of Impurities near Liquid - Stagnant layer interface} \).

Hence uniform of Doping in Crystal is Possible if Pull rate \( R \) is High
and Spin is Slow \( \delta \propto \frac{1}{\text{Spin speed}} \)
In the float zone process, dopants and other impurities tend to stay in the liquid and therefore refining can be accomplished, especially with multiple passes.

See the text for models of this process.
Oxygen and Carbon in CZ Silicon

- The CZ growth process inherently introduces O and C.
- Typically, $C_O \approx 10^{18}$ cm$^{-3}$ and $C_C \approx 10^{16}$ cm$^{-3}$.
- The O in CZ silicon often forms small SiO$_2$ precipitates in the Si crystal under normal processing conditions.

- Oxidation of silver in CZ silicon can actually be very useful.
  - Provide mechanical strength.
  - Internal gettering (described later in Chapter 4).