Crystal Growth

1. Czochralaki 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 very high degree of uniformity of Impurities of choice (Dopants).

(d) Highly pure Silicon wafers with impurities like O, C & Fe etc absent

(e) Resistivities of the Order of 10000 ohm-cm and even 20000 ohmcm are possible. Compared to CZ crystals which can high 100 Ωcm resistivity.

1 Doping — P or n type

2 Crystal Orientation $\langle 100 \rangle$

3. Resistivity 0.1 ohmcm → 0.1 to 0.9 ohmcm.

4 Dislocation Count : no of dislocations/cm2
EDP

5 radial resistivity variation.

6 Thickness

7 Diameter ± ΔD

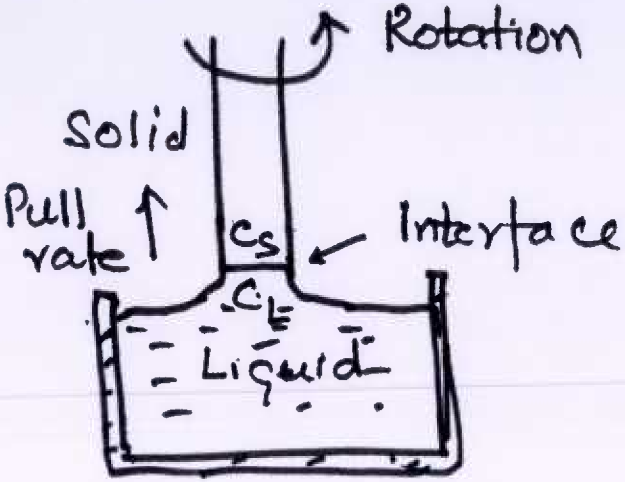
Modeling Dopant Behaviour During Crystal Growth – Mathematical Representation

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

$$\text{Segregation Coeff. } k_0 = \frac{C_S}{C_L} = \frac{\text{Conc. of Solute (By Wt) in Solid}}{\text{Conc. of Solute (By Wt.) in Liquid}}$$

CZ Process (cont.)



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

Dopant/Impurity	Segregation Coeff. k
B	0.8
Al	2.8×10^{-3}
Ga	8×10^{-3}
In	3.6×10^{-4}
P	0.35
As	0.30
Sb	0.023
O	0.5
C	0.07
Li	10^{-2}
Bi	7×10^{-4}
Au	2.5×10^{-5}

If C_S = Conc. of Impurities in Solid surface (By Wt)

& C_L = Conc. of Impurities in Liquid (Melt)(By Wt.)

One defines segregation Coefficient k_o as

$$k_o = \frac{C_S}{C_L}$$

Rapid Stirring Case:

Let W_M = Initial Weight of Melt

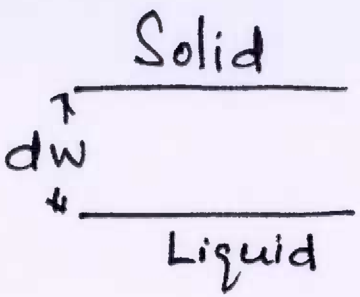
C_M = Conc. of Solute in Melt (By Wt.)

During Crystal Growth, at any Instant

C_L = conc. of Solute in Liquid

C_S = conc. of Solute in Solid

One defines S as weight of Solute in Melt



Consider 'dw' is wt. of an element of a Crystal of thickness $\rightarrow dW$

$\therefore$ Weight of Solute lost from melt $S = dS$

$$\therefore \quad dS = -C_S\,dW$$

At this Instant of time

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

$$\therefore \quad \text{Conc. } C_L = \frac{S}{W_M - W}$$

Please note that at Initial time

C_M = Conc. of Solute in Melt

& W_M = Weight of Melt

$\therefore$ Weight of Solute at $t=0$

$$S_0 = C_M \cdot W_M$$

As $k_0 = \dfrac{C_S}{C_L}$, we have

$$dS = -C_S\,dW$$

$$\therefore\ ds = -k_0 C_L\, dW$$

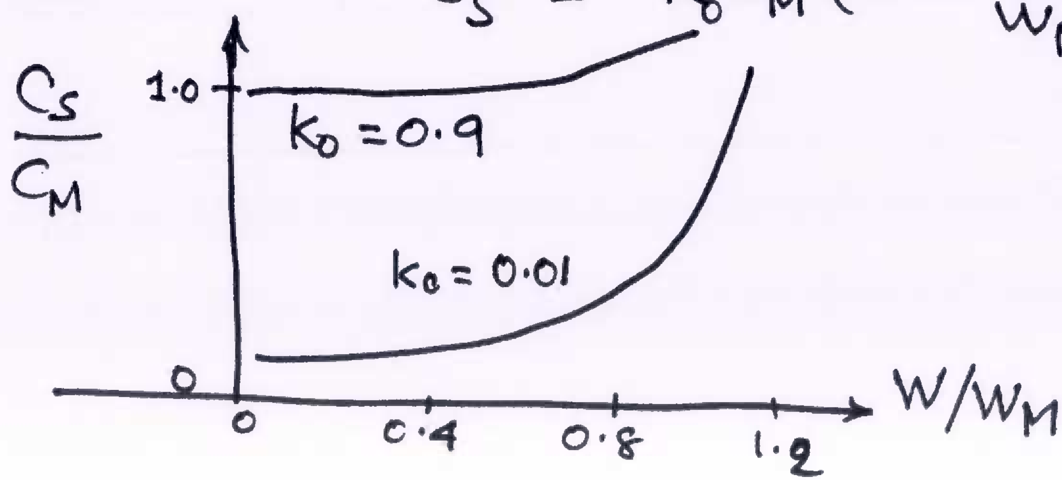
$$= -k_0 \frac{S}{W_M - W} \cdot dW$$

$$\text{or}\quad \frac{dS}{S} = -k_0 \frac{dW}{W_M - W}$$

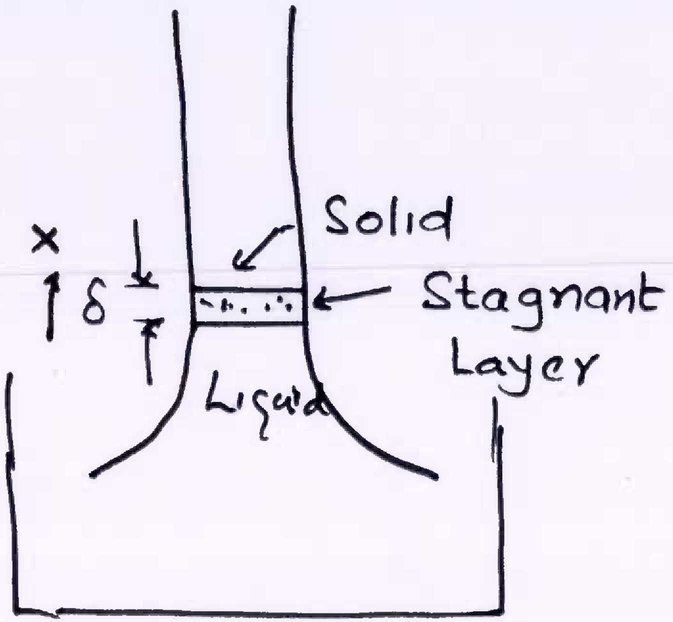
$$\therefore\ \int_{S_0}^{S} \frac{dS}{S} = -k_0 \int_0^W \frac{dW}{W_M - W}$$

$S_0 = W_M C_M$

$$\therefore\ C_S = k_0 C_M \left(1 - \frac{W}{W_M}\right)^{k_0 - 1}$$



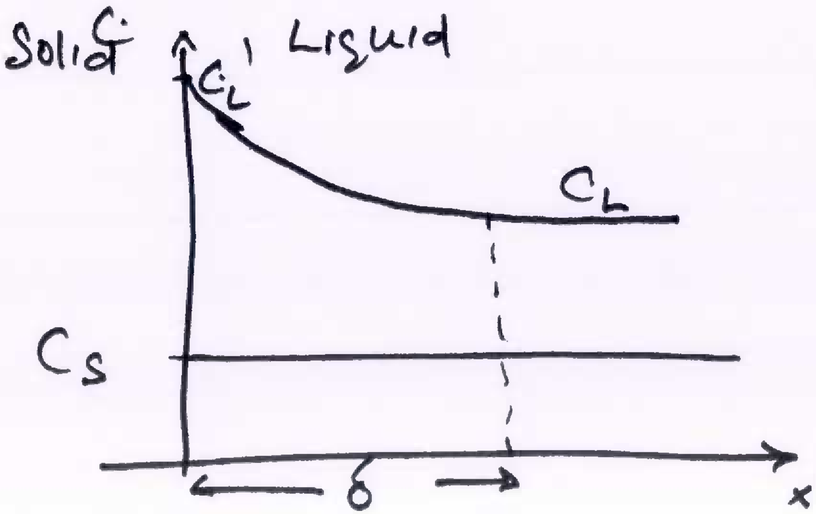
Partial - Stirring Cond's



Slow Stirring Creates a Stagnant Layer of thickness 'δ' between Solid & Liquid.

The dopant diffuses through the Stagnant layer (δ) 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

& D = Diffusion coefficient of Solute atoms in the Liquid (Top portion of Melt)

Typically $D = 5\times10^{-5}\ cm^2/sec$ 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

$$C = A e^{-Rx/D} + B$$

$$\therefore \frac{dc}{dx} = -\frac{AR}{D} e^{-Rx/D}$$

Boundary Cond^{n}s : (i) $C = C_L'$ at $x = 0$

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

The equivalent coeff $k_e = \dfrac{C_S}{C_L}$ & $k_0 = \dfrac{C_S}{C_L'}$

It is found that $k_e = C_S/C_L$ which is now

$$k_e = \frac{k_0}{k_0 + (1-k_0)\,e^{-\frac{R\delta}{D}}}$$

Here $k_0 = \dfrac{C_S}{C_L'}$

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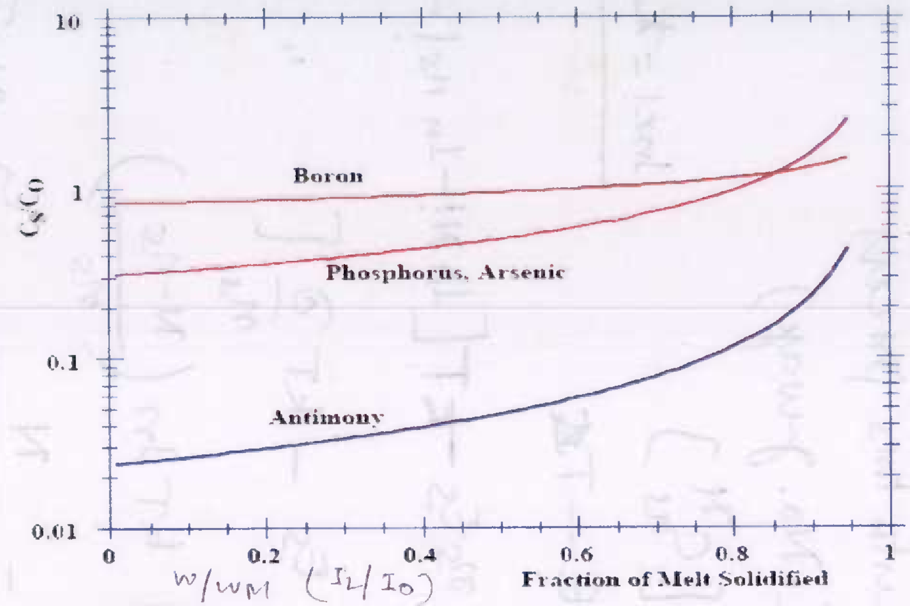
where R = Rate of growth of Crystal

D = 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

$$\delta \propto \frac{1}{\text{Spin speed}}$$

Float Zone Process



Zone leveling

$C_s = k_e C_0 e^{-k_e x/L}$

L – Molten zone length.

C_0 = doping conc in melt

$dS = C_M A \rho\, dx - \frac{k_e S}{L} dx$

At equilibrium at x=0

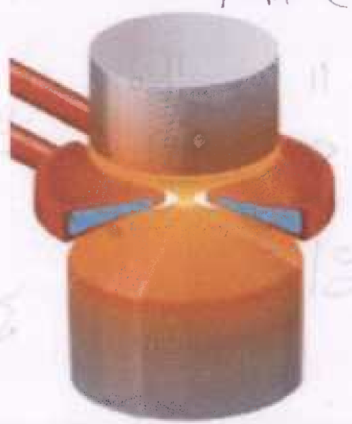
$S = C_M A \rho L$

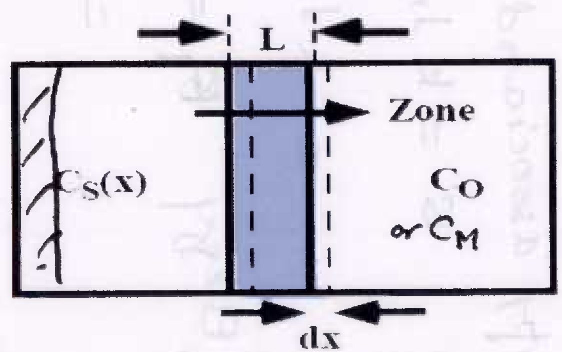
$\therefore S = \frac{C_M A \rho}{k_e} \times \left[1-(1-k_e)e^{-\frac{k_e x}{L}}\right]$

↓

$C_s = C_M [\quad]$

$C_s = \frac{k_e S}{A \rho L}$





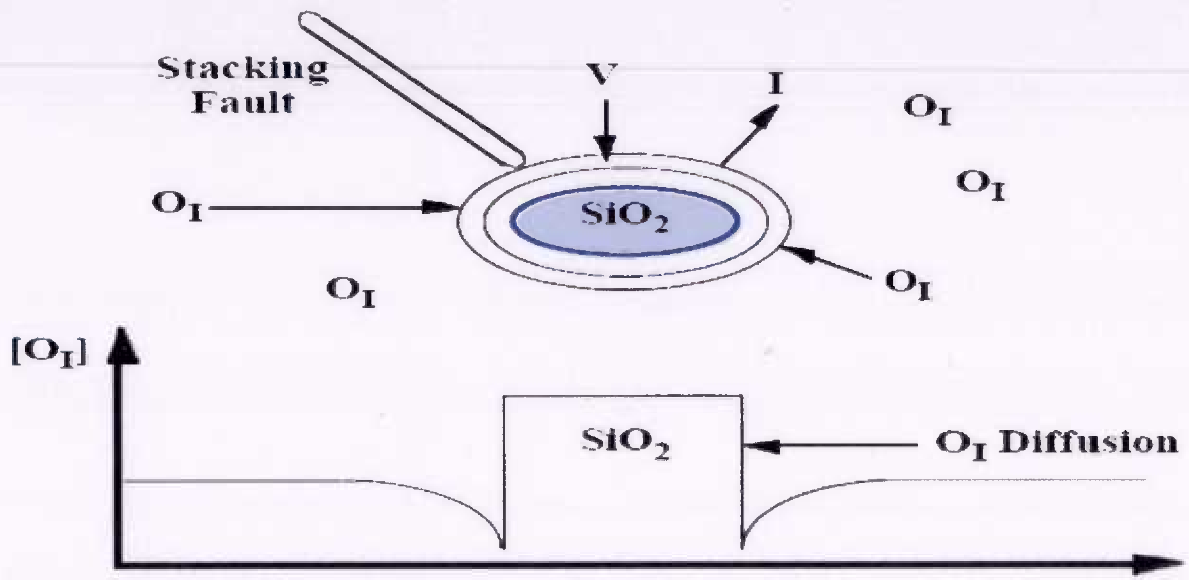
(Left - Mitsubishi website at http://www.egg.or.jp/MSIL/english/index-e.html)

- 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.

Plummer

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.



- O and these precipitates can actually be very useful.
  - Provide mechanical strength.
  - Internal gettering (described later in Chapter 4).

Plummer