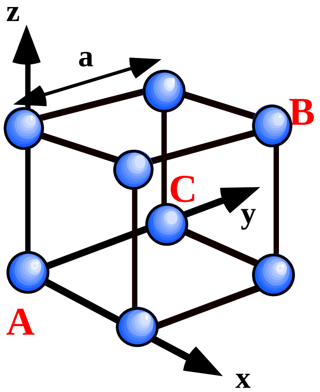
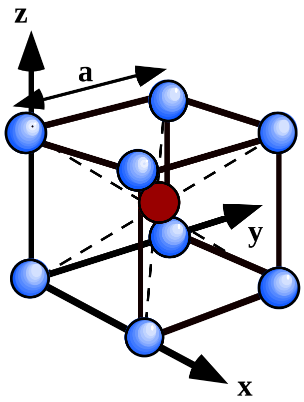
EE 212 FALL 1999-00

CRYSTAL GROWTH, WAFER FABRICATION AND BASIC PROPERTIES OF Si WAFERS- Chapter 3

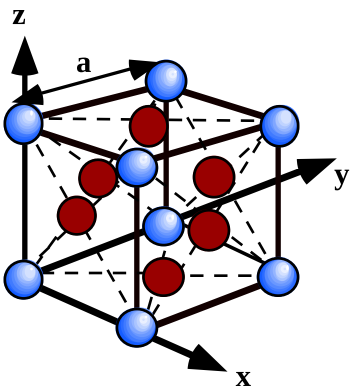
Crystal Structure



Cubic

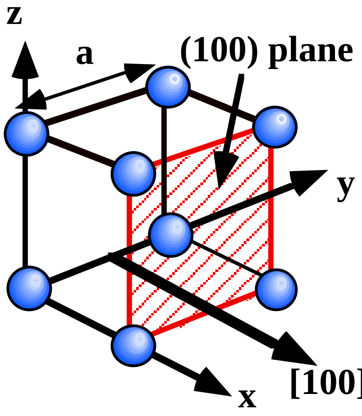


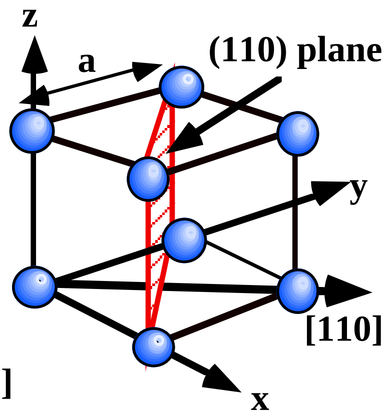
BCC

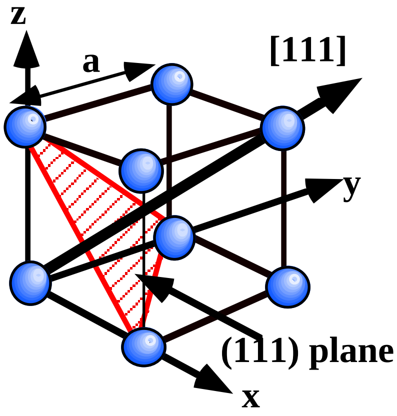


FCC

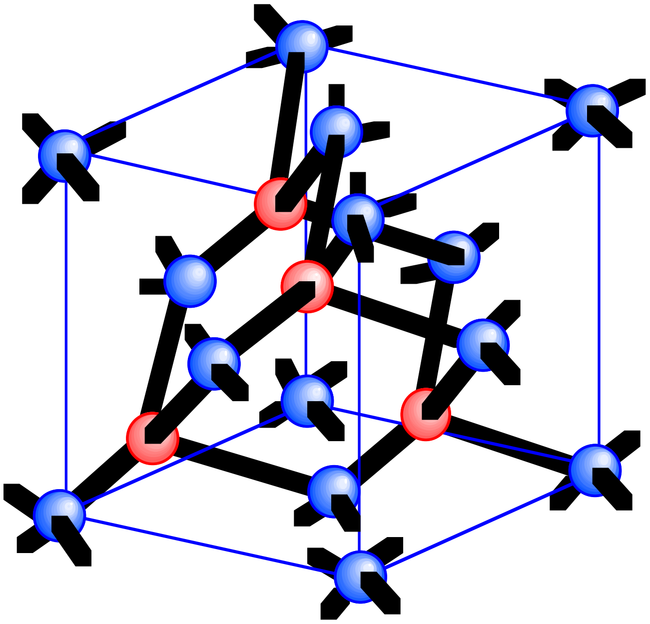
- Crystals are characterized by a unit cell which repeats in the x, y, z directions.



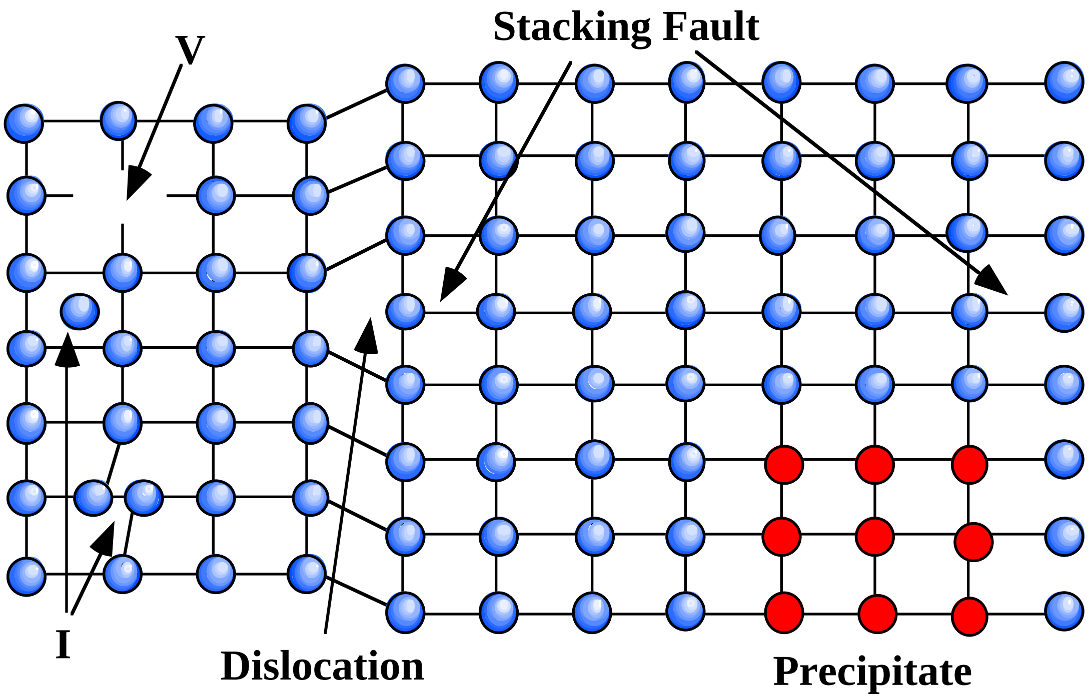




- Planes and directions are defined using an x, y, z coordinate system.
- [111] direction is defined by a vector having components of 1 unit in x, y and z.
- Planes are defined by Miller indices - reciprocals of the intercepts of the plane with the x, y and z axes.



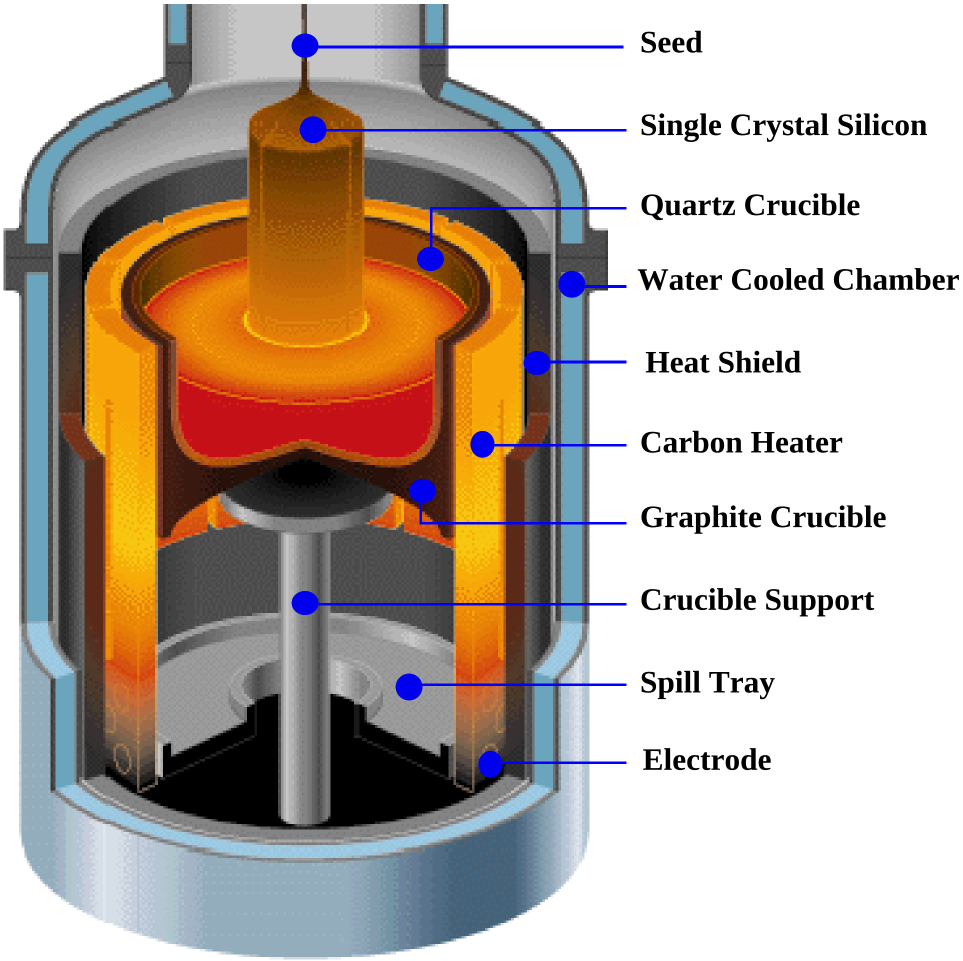
- **Silicon has the basic diamond crystal structure - two merged FCC cells offset by a/4 in x, y and z.**



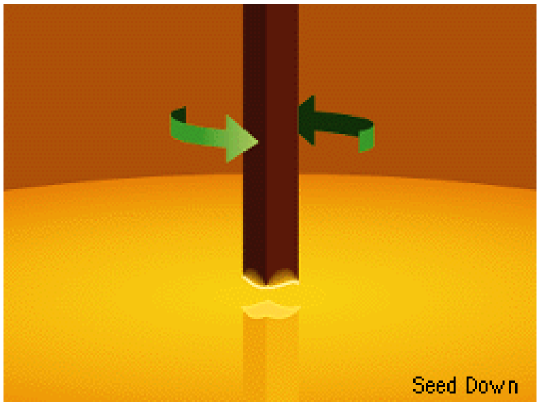
- **Various types of defects can exist in crystal (or can be created by processing steps. In general these are detrimental to device performance.**

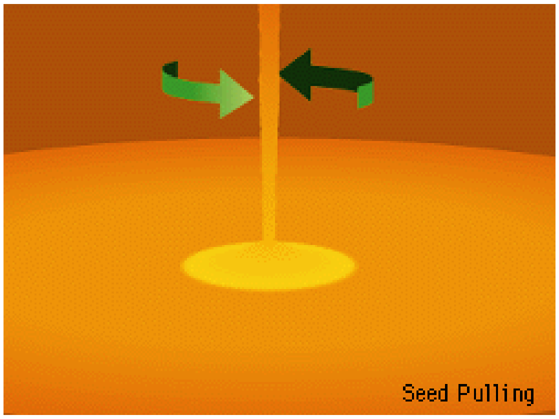
Crystal Growth

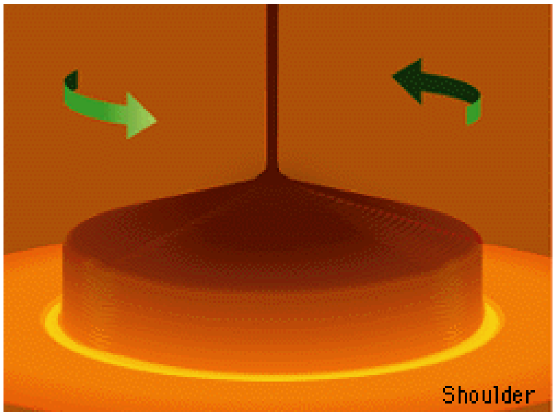
- The raw Si used for crystal growth is purified from SiO_2 (sand) through refining, fractional distillation and CVD.
- The raw material contains < 1 ppb impurities except for O ($\approx 10^{18}$ cm^{-3}) and C ($\approx 10^{16}$ cm^{-3})

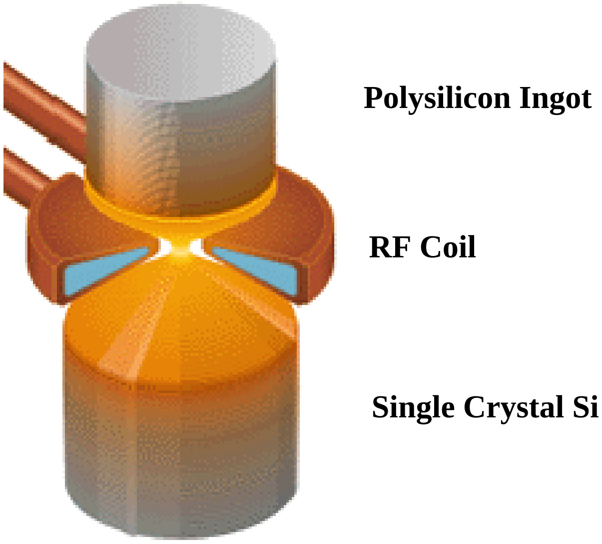


- Essentially all Si wafers used for ICs today come from Czochralski grown crystals.
- Polysilicon material is melted, held at close to 1415 ˚C, and a single crystal seed is used to start the crystal growth.
- Pull rate, melt temperature and rotation rate are all important control parameters.

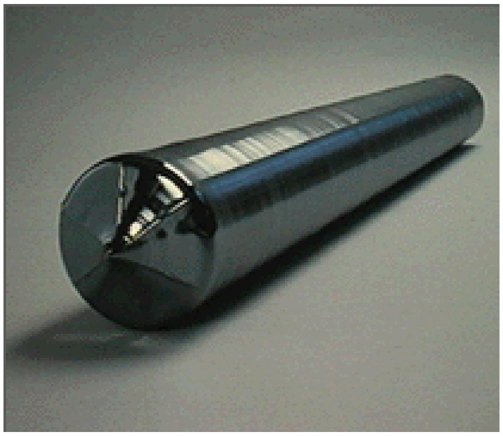


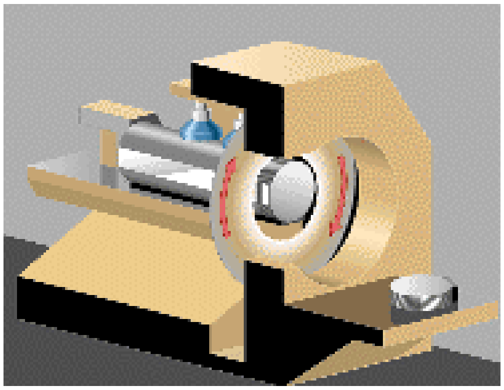






- **An alternative growth process is the float zone process which can be used for either refining or single crystal growth.**



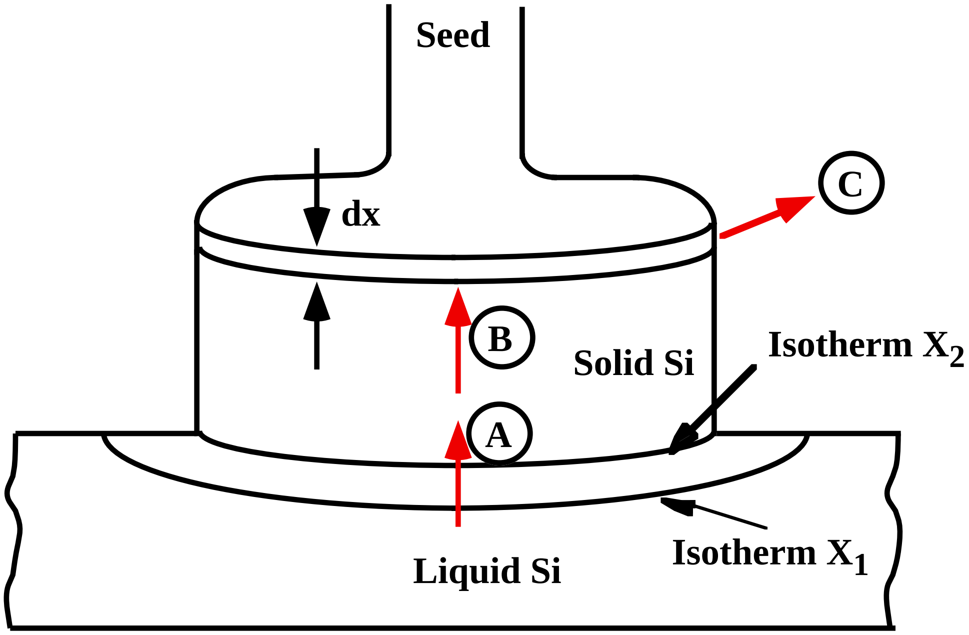


- **After crystal pulling, the boule is shaped and cut into wafers which are then polished on one side.**

- **The details of these processes are described in the text.**

Modeling Crystal Growth

- **We wish to find a relationship between pull rate and crystal diameter.**



- **Freezing occurs between isotherms X_1 and X_2.**

- **Heat balance: latent heat of crystallization + heat conducted from melt to crystal = heat conducted away.**

$$L\frac{dm}{dt} + k_L\frac{dT}{dx_1}A_1 = k_S\frac{dT}{dx_2}A_2 \qquad (1)$$

where:

$L =$ **latent heat of fusion**

$\frac{dm}{dt} =$ **amount of freezing per unit time**

$k_L =$ **thermal conductivity of liquid**

$\frac{dT}{dx_1} =$ **thermal gradient at isotherm** x_1

$k_S =$ **thermal conductivity of solid**

$\frac{dT}{dx_2} =$ **thermal gradient at** x_2

- **The rate of growth of the crystal is**

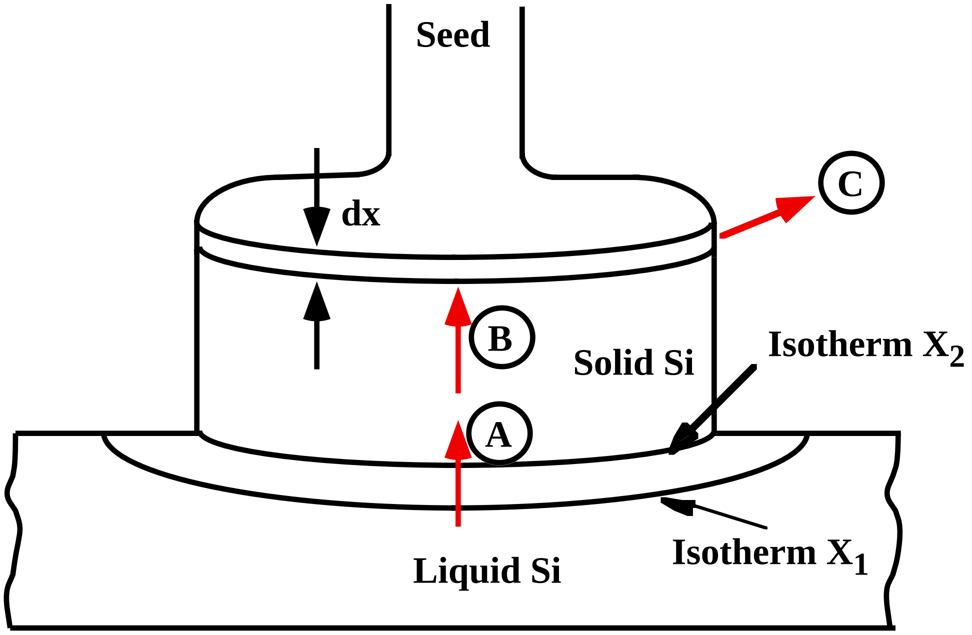
$$\frac{dm}{dt} = v_P AN \qquad (2)$$

where v_P is the pull rate and N is the density.

- **Neglecting the middle term in Eqn. (1) and substituting,**

$$v_{PMAX} = \frac{k_S}{LN}\frac{dT}{dx_2} \qquad (3)$$

- **In order to replace dT/dx_2, we need to consider the heat transfer processes.**



- **Heat radiation from the crystal (C) is given by the Stefan-Boltzmann law**

$$dQ = (2\pi r dx)\left(\sigma \varepsilon T^4\right) \tag{4}$$

- **Heat conduction up the crystal is given by**

$$Q = k_S\left(\pi r^2\right)\frac{dT}{dx} \tag{5}$$

- **Differentiating (5), we have**

$$\frac{dQ}{dx} = k_S\left(\pi r^2\right)\frac{d^2T}{dx^2} + \left(\pi r^2\right)\frac{dT}{dx}\frac{dk_S}{dx} \cong k_S\left(\pi r^2\right)\frac{d^2T}{dx^2} \tag{6}$$

- **Substituting (6) into (4), we have**

$$\frac{d^2T}{dx^2} - \frac{2\sigma\varepsilon}{k_S r} T^4 = 0 \qquad (7)$$

- **k_S varies roughly as 1/T, so if k_M is the thermal conductivity at the melting point,**

$$k_S = k_M \frac{T_M}{T} \qquad (8)$$

$$\therefore \frac{d^2T}{dx^2} - \frac{2\sigma\varepsilon}{k_M r T_M} T^5 = 0 \qquad (9)$$

- **Solving this differential equation, evaluating it at x = 0 and substituting the result into (3), we obtain: (see text)**

$$v_{PMAX} = \frac{1}{LN}\sqrt{\frac{2\sigma\varepsilon k_M T_M^5}{3r}} \qquad (10)$$

- **This gives a max pull rate of ≈ 35 cm hr^{-1} for a 6" crystal. Actual values are ≈ 2X less than this.**

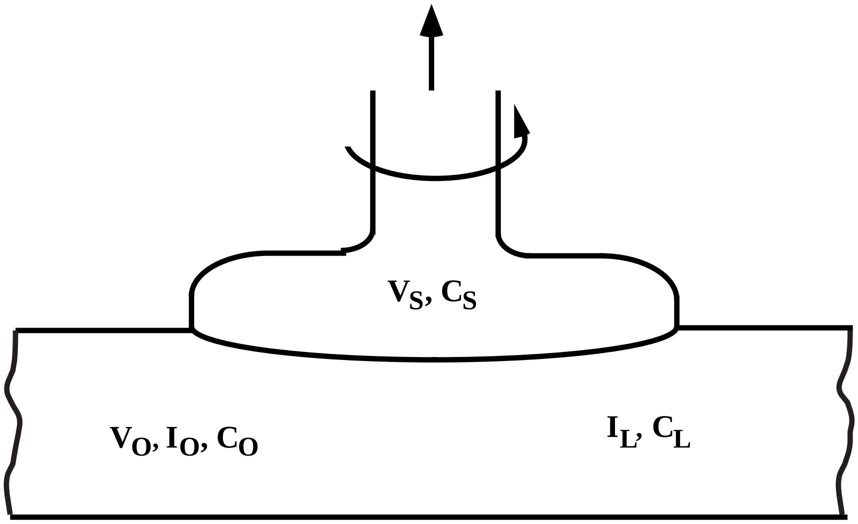
Modeling Dopant Behavior During Crystal Growth

- **Dopants are added to the melt to provide a controlled N or P doping level in the wafers.**
- **However, the dopant incorporation process is complicated by dopant segregation.**

$$k_O = \frac{C_S}{C_L} \qquad (11)$$

As	**0.3**
Bi	**7×10^{-4}**
C	**0.07**
Li	**10^{-2}**
O	**0.5**
P	**0.35**
Sb	**0.023**
Al	**2.8×10^{-3}**
Ga	**8×10^{-3}**
B	**0.8**
Au	**2.5×10^{-5}**

- **Most k_0 values are <1 which means the impurity prefers to stay in the liquid.**
- **Thus as the crystal is pulled, N_S will increase.**



- **If during growth, an additional volume dV freezes, the impurities incorporated into dV are given by**

$$dI = -k_O C_L dV = -k_O \frac{I_L}{V_O - V_S} dV \qquad (12)$$

$$\therefore \int_{I_O}^{I_L} \frac{dI}{I_L} = -k_O \int_0^{V_S} \frac{dV}{V_O - V_S} \qquad \textbf{(13)}$$

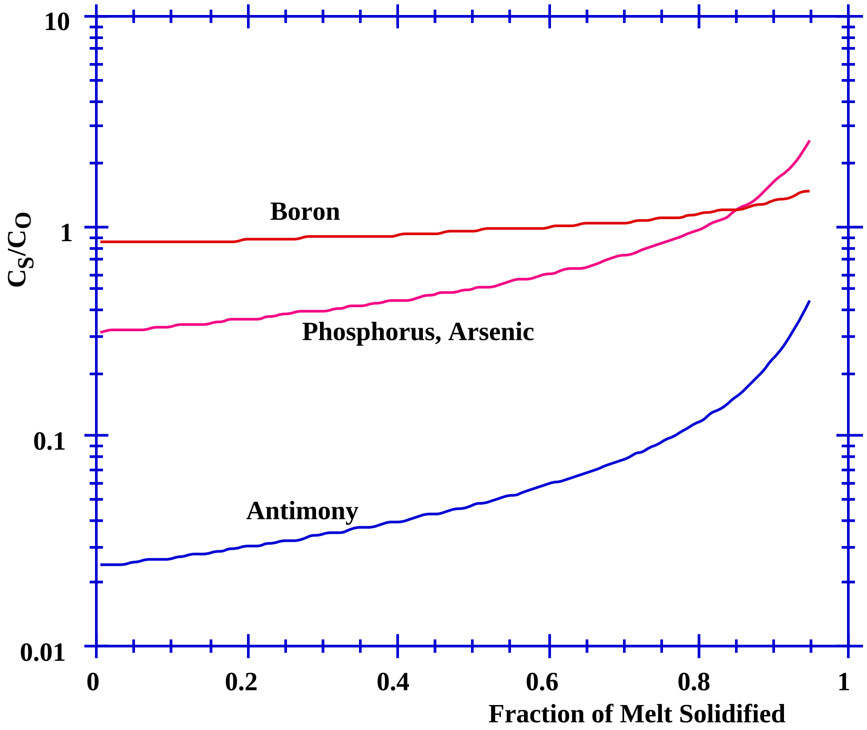
$$\therefore I_L = I_O\left(1 - \frac{V_S}{V_O}\right)^{k_O} \qquad \textbf{(14)}$$

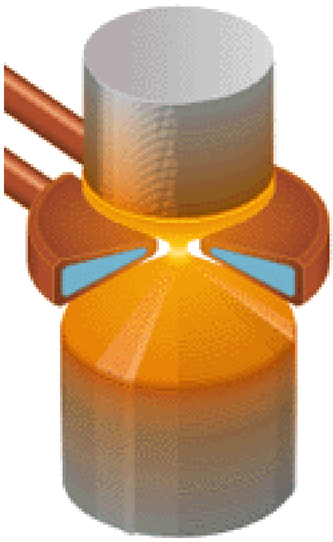
- **We are really interested in the impurity level in the crystal (C_S), so that**

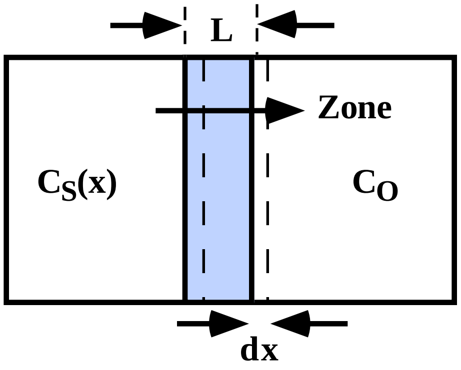
$$C_S = \frac{dI_L}{dV_S} \qquad \textbf{(15)}$$

$$\therefore C_S = C_O k_O (1 - f)^{k_O - 1} \qquad \textbf{(16)}$$

where f is the fraction of the melt frozen.







- **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.**

Modeling Point Defects in Silicon

- **Point defects (V and I) will turn out to play fundamental roles in many process technologies.**
- **The total free energy of the crystal is minimized when finite concentrations of these defects exist.**

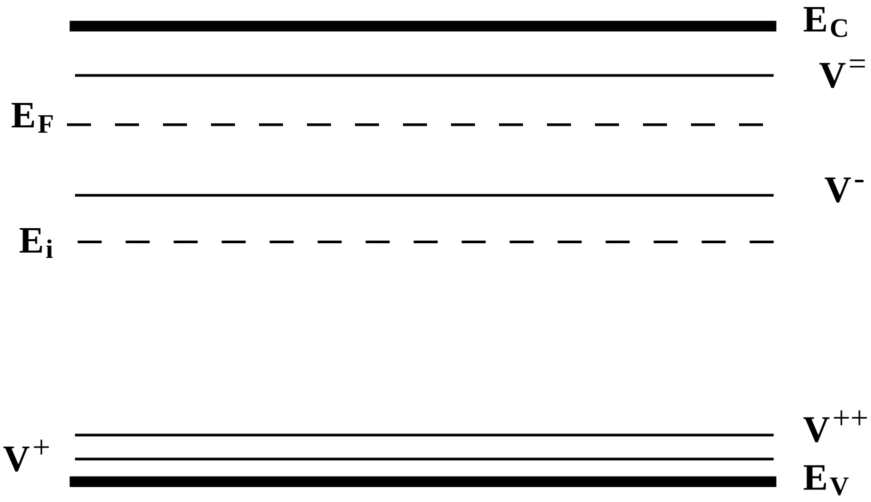
$$C^*_{I^0}\ ,\ C^*_{V^0} = N_S \exp\left(\frac{S^f}{k}\right)\exp\left(\frac{-H^f}{kT}\right) \qquad (17)$$

- **In general $C^*_{I^0} \neq C^*_{V^0}$ and both are strong functions of temperature.**
- **Kinetics may determine the concentration in a wafer rather than thermodynamics.**
- **In equilibrium, values for these concentrations are given by:**

$$C^*_{I^0} \cong 1\mathrm{x}10^{27} \exp\left(\frac{-3.8\mathrm{eV}}{kT}\right) \qquad (18)$$

$$C^*_{V^0} \cong 9\mathrm{x}10^{23} \exp\left(\frac{-2.6\mathrm{eV}}{kT}\right) \qquad (19)$$

- **These equations give $C^*_{I^0}$ & $C^*_{V^0} \approx 0$ at room T and 10^{12} - 10^{14} cm^{-3} at 1000 °C - too small to measure.**



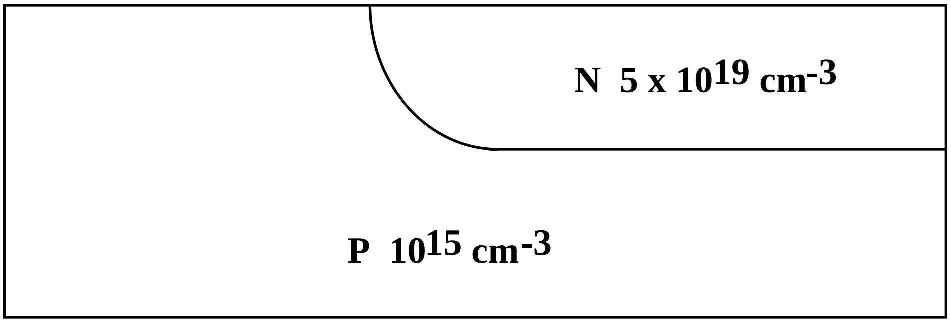
- **V and I also exist in charged states with discrete energies in the Si bandgap.**
- **In N type Si, $V^=$ and V^- will dominate; in P type, V^+ and V^{++} will dominate.**
- **Shockley and Last (1957) first described these charged defect concentrations (see text):**

$$C^*_{V^+} = C^*_{V^0} \exp\left(\frac{E_{V^+} - E_F}{kT}\right) \qquad (20)$$

$$C^*_{V^-} = C^*_{V^0} \exp\left(\frac{E_F - E_{V^-}}{kT}\right) \qquad (21)$$

- Note that:
  - The defect concentrations are always $<< n_i$. (∴ doping → E_F → point defect concentrations)
  - As doping changes, the neutral point defect concentrations are constant.
  - However, the charged defect concentrations change with doping. ∴ the total point defect concentrations change with doping.

Example: (See text for details)



- At 1000 °C, the P region will be intrinsic, the N region is extrinsic.

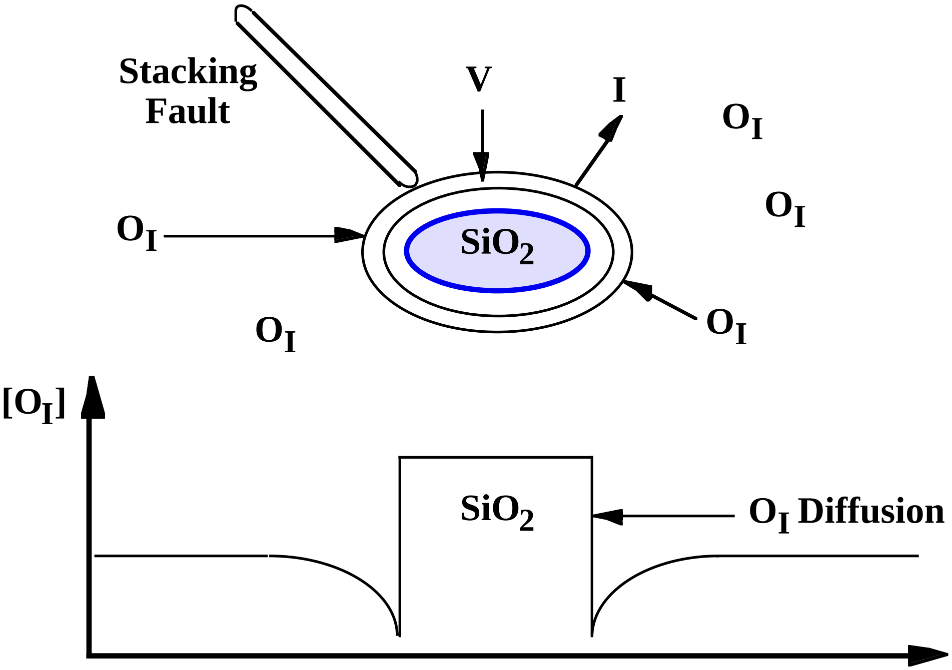
	P Region	N Region
Doping	1 x 10^{15} cm^{-3}	5 x 10^{19} cm^{-3}
n_i	7.14 x 10^{18} cm^{-3}	7.14 x 10^{18} cm^{-3}
V^0	4.6 x 10^{13} cm^{-3}	4.6 x 10^{13} cm^{-3}
V^-	2.37 x 10^{14} cm^{-3}	1.61 x 10^{15} cm^{-3}
$V^=$	1.85 x 10^{13} cm^{-3}	8.50 x 10^{14} cm^{-3}
V^+	2.08 x 10^{12} cm^{-3}	3.06 x 10^{11} cm^{-3}
V^{++}	1.94 x 10^{11} cm^{-3}	4.23 x 10^{9} cm^{-3}
I^0	9.13 x 10^{11} cm^{-3}	9.13 x 10^{11} cm^{-3}
I^-	4.02 x 10^{11} cm^{-3}	2.73 x 10^{12} cm^{-3}
I^+	8.32 x 10^{10} cm^{-3}	1.48 x 10^{11} cm^{-3}

Note:

  - n_i relative to doping in the two regions.
  - V^0 is the same in the two regions.
  - Different charge states dominate in the different regions.
- The concentrations of these point defects will be important later in the quarter (diffusion, ion implantation, oxidation models).

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 (Chapter 4 - later).
- See the text (Chapter 3) for more detailed information.