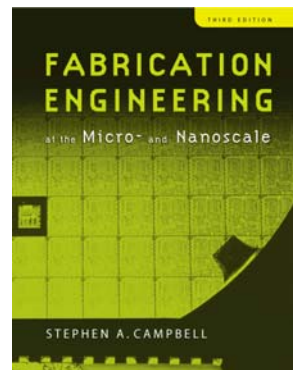


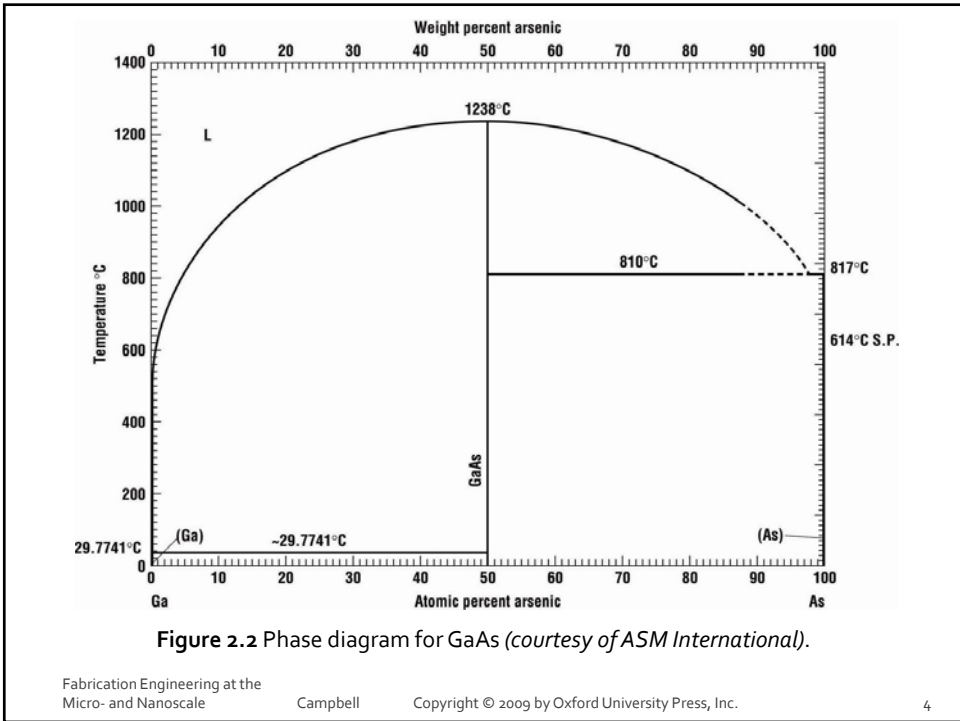
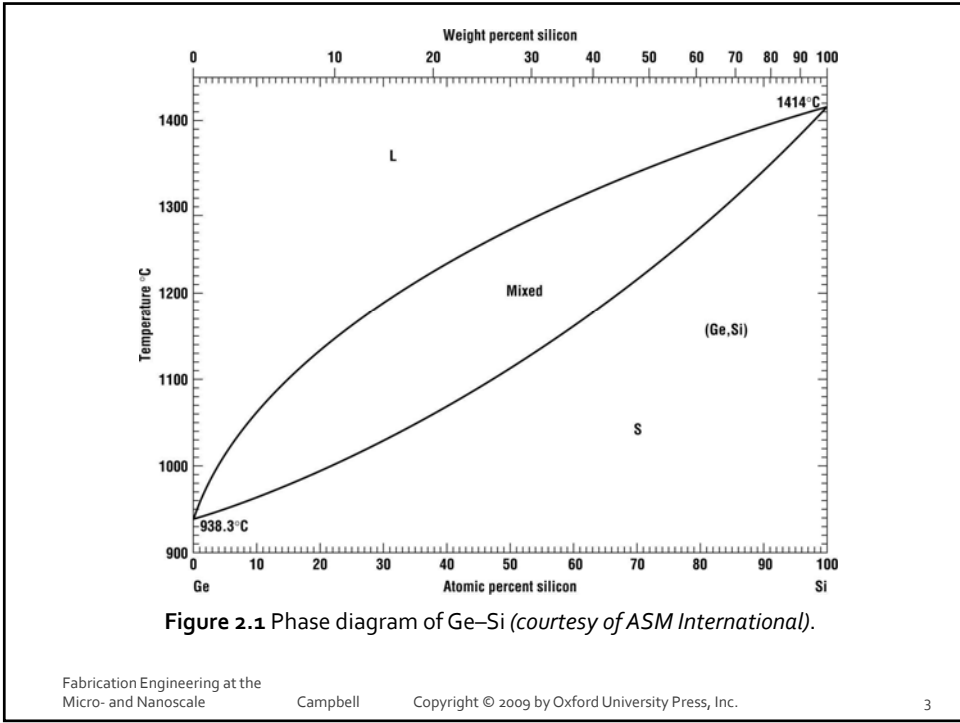
# ECE 416/516 IC Technologies Lecture 2: Semiconductor Substrates

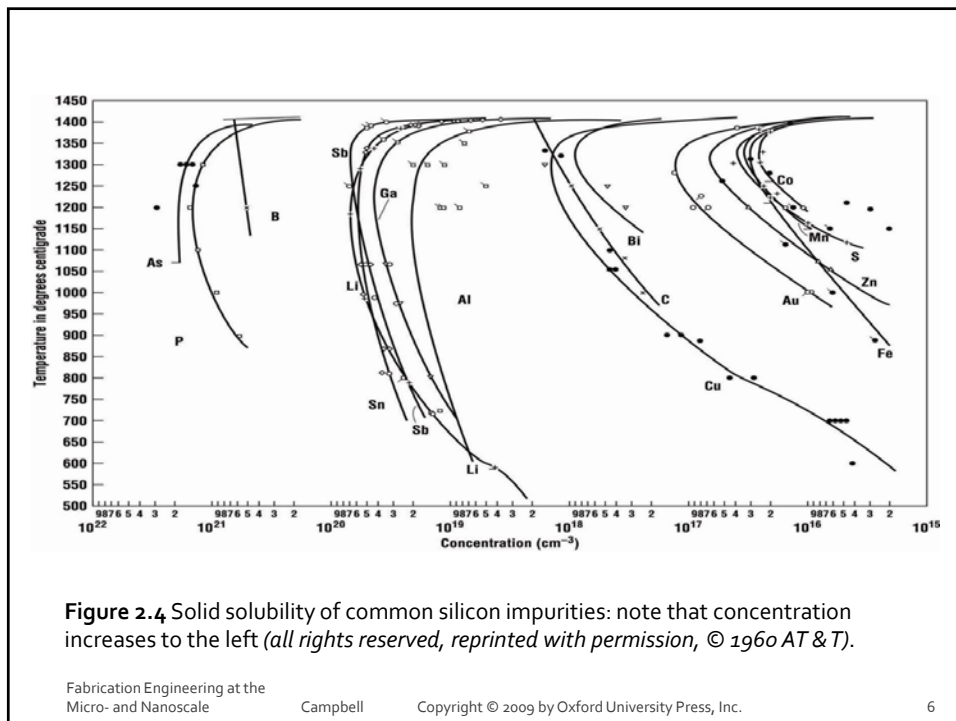
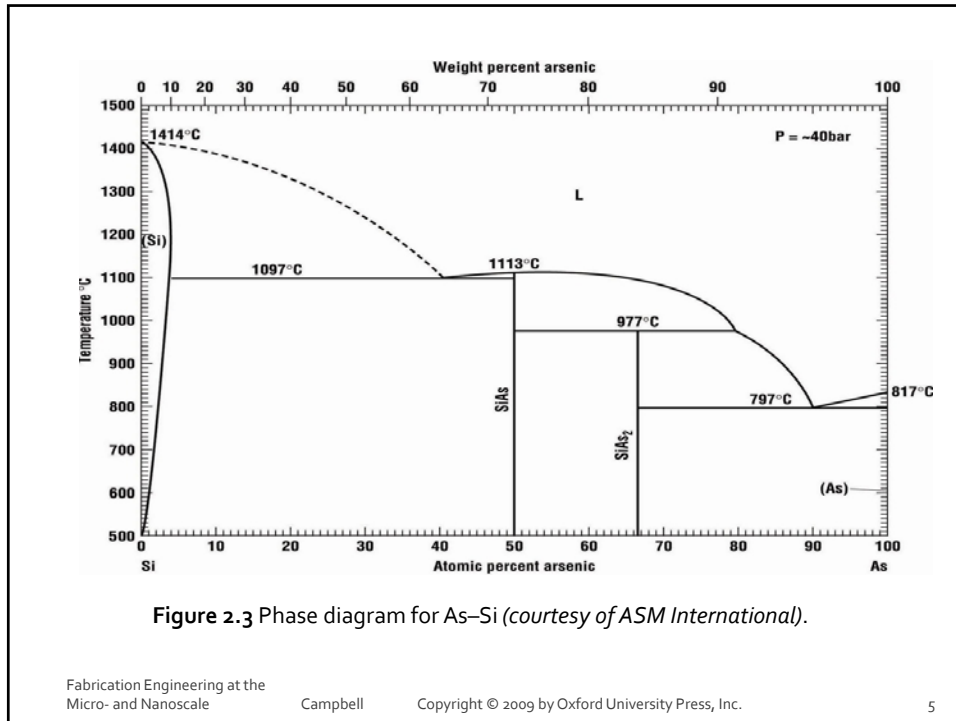
Professor James E. Morris  
Spring 2012

## Chapter 2

### Semiconductor Substrates

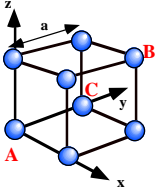




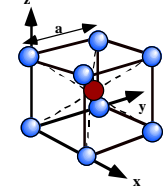


### CRYSTAL GROWTH, WAFER FABRICATION AND BASIC PROPERTIES OF Si WAFERS-

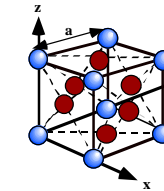
#### Crystal Structure



Cubic

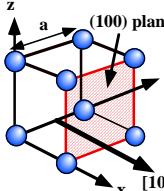


BCC

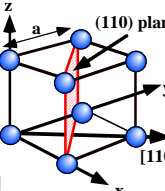


FCC

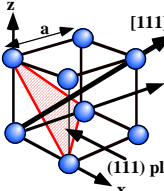
- Crystals are characterized by a unit cell which repeats in the x, y, z directions.



(100) plane



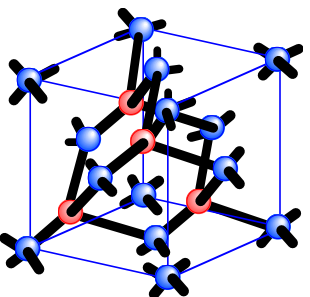
(110) plane



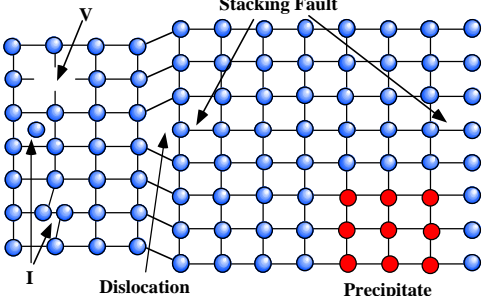
[111]  
(111) plane  
[110]

- 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.

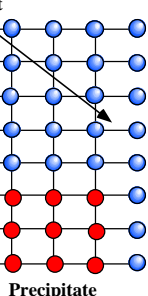
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- Silicon has the basic diamond crystal structure - two merged FCC cells offset by  $a/4$  in x, y and z. See 3D models <http://jas.eng.buffalo.edu/education/solid/unitCell/home.html>



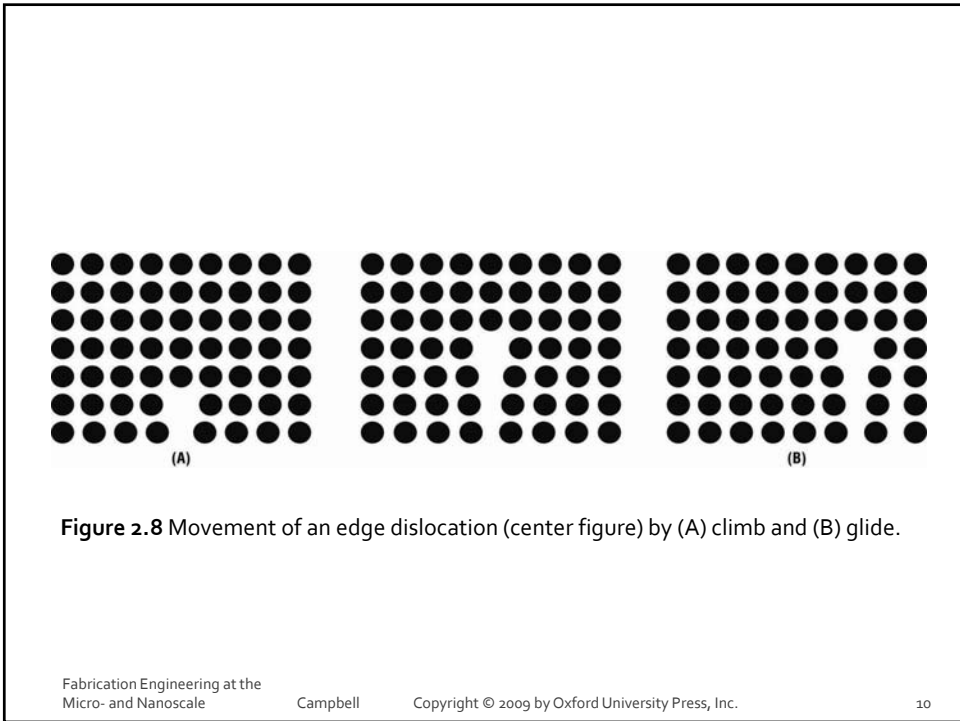
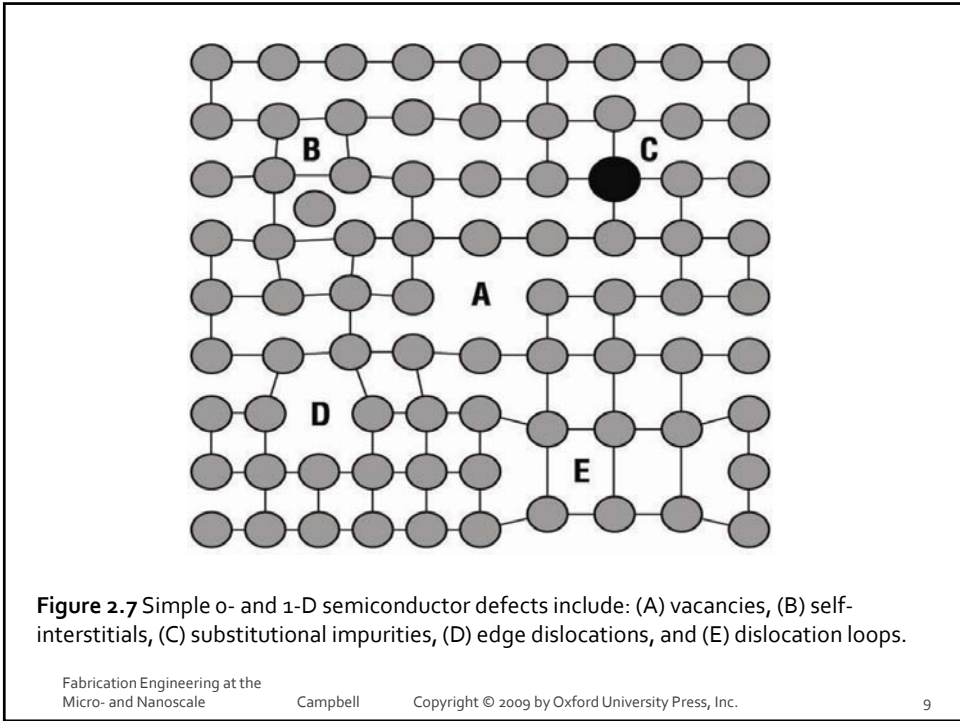
Dislocation

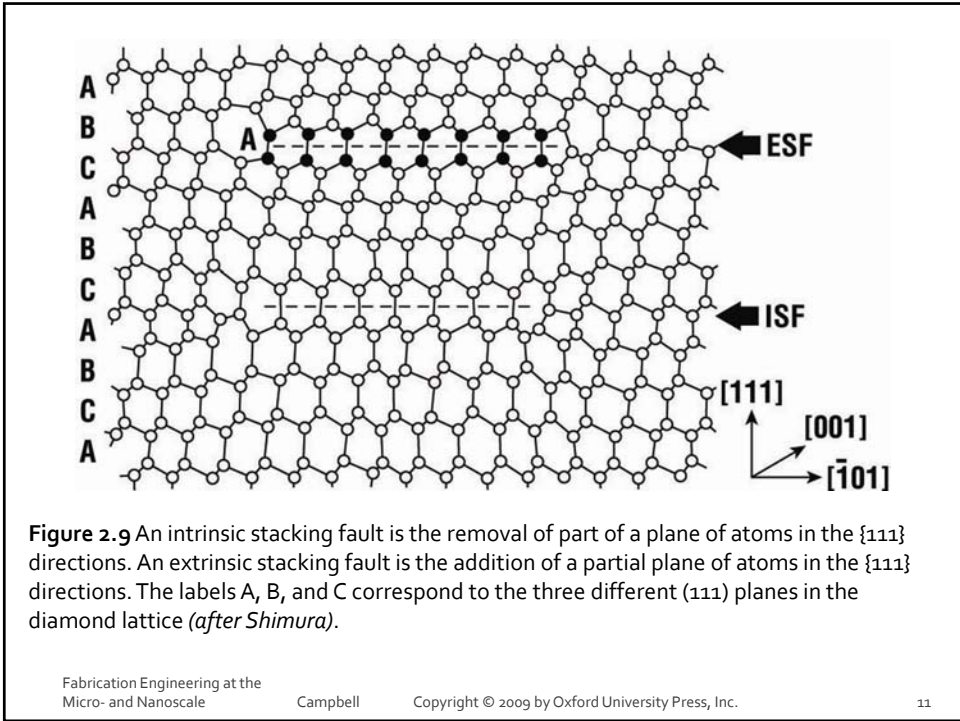


Precipitate

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

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### 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.

$$C_I^*, C_V^* = N_S \exp\left(\frac{S^f}{k}\right) \exp\left(\frac{-H^f}{kT}\right) \quad (17)$$

- In general  $C_I^* \neq C_V^*$  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:

$$C_I^* \cong 1 \times 10^{27} \exp\left(\frac{-3.8\text{eV}}{kT}\right) \quad (18)$$

$$C_V^* \cong 9 \times 10^{23} \exp\left(\frac{-2.6\text{eV}}{kT}\right) \quad (19)$$

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• V and I also exist in charged states with discrete energies in the Si bandgap.

• In N type Si, V<sup>0</sup> and V<sup>-</sup> will dominate; in P type, V<sup>+</sup> and V<sup>++</sup> will dominate.

• Shockley and Last (1957) first described these charged defect concentrations.

Note: • The defect concentrations are always  $\ll n_i$ . (doping  $\rightarrow E_F \rightarrow$  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.

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

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

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**Example:**

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

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

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.

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## Production of Industrial Grade Si

### 1. SiO<sub>2</sub> reduction in electric furnace



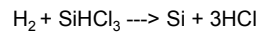
95-97% purity

Refine to 11N(?)EGS

(electronic grade polysilicon)

### 2. Siemens process (Si CVD from TCS)

(tri-chlorosilane)



Homogeneous reaction in gas  $\rightarrow$  Si deposits on walls

Heterogeneous reaction on heated Si rod

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## EGS Production

Steel industry by-product MGS (Metallurgical Grade Solution)

↓ - HCl from Siemens Process

TCS

↓ - Purify by distillation, etc

Pure TCS

↓ - Siemens Process

EGS

↓ - Czochralski Process

Single Crystal Si

↓ - Saw and Polish

Wafers

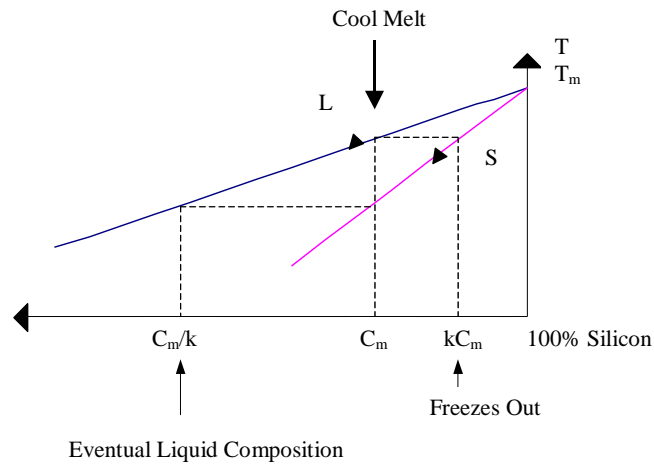
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## Impurity Doping: Phase Diagram



Note: Doping density in melt increases as crystal drawn

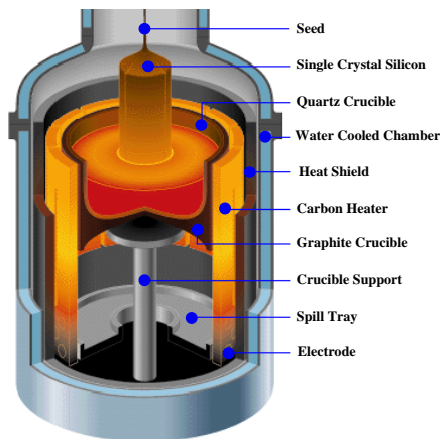
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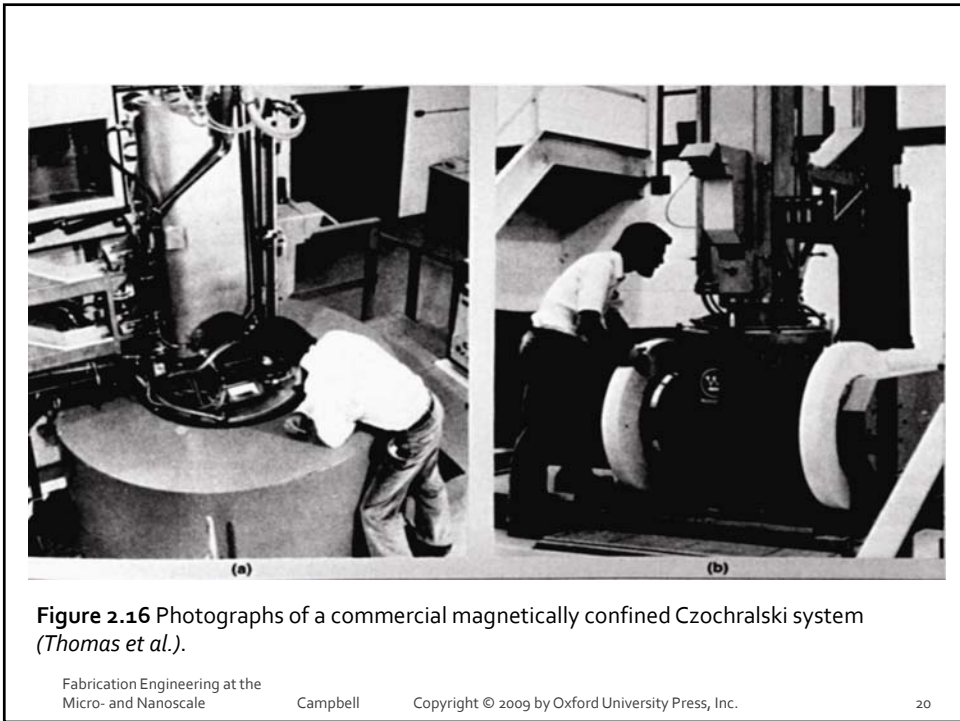
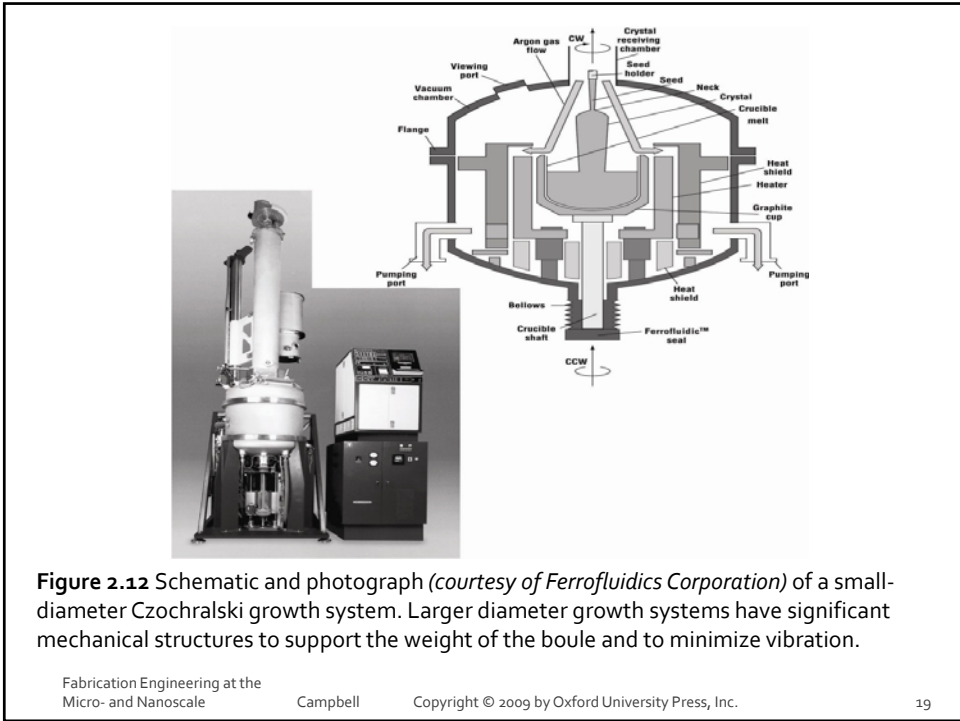
## Crystal Growth

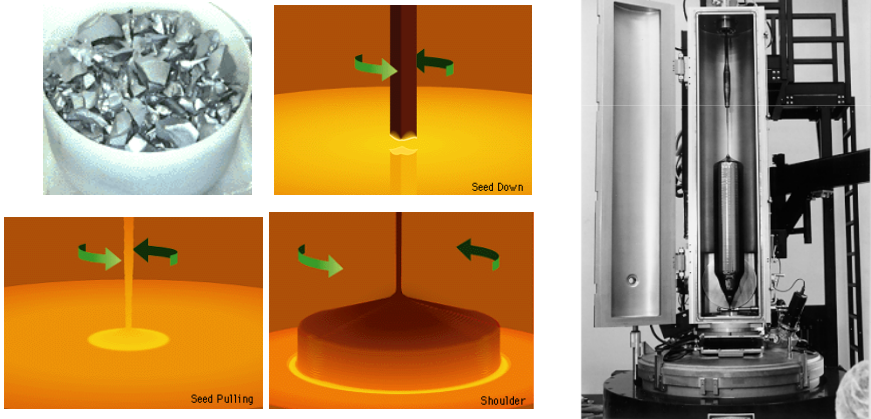
- Si used for crystal growth is purified from  $\text{SiO}_2$  (sand) through refining, fractional distillation and CVD.
- The raw material contains  $< 1$  ppb impurities. Pulled crystals contain O ( $\approx 10^{18} \text{ cm}^{-3}$ ) and C ( $\approx 10^{16} \text{ cm}^{-3}$ ), plus any added dopants placed in the melt.



- Essentially all Si wafers used for ICs today come from Czochralski grown crystals.
- Polysilicon material is melted, held at close to  $1417^\circ\text{C}$ , and a single crystal seed is used to start the growth.
- Pull rate, melt temperature and rotation rate are all important control parameters.

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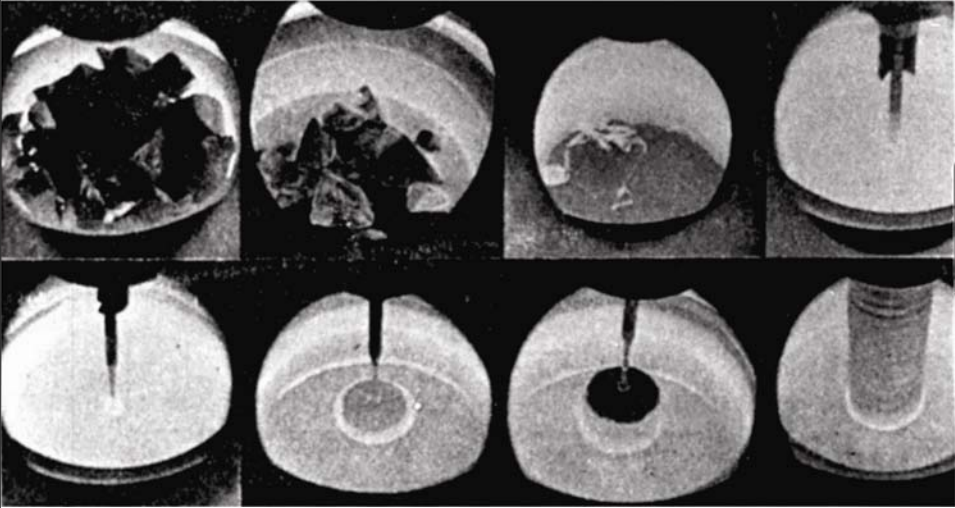




The figure illustrates the Czochralski crystal growth process. On the left, a bowl contains a mixture of raw materials. The central part consists of three diagrams: 'Seed Down' shows a seed crystal being lowered into a melt; 'Seed Pulling' shows the seed being slowly pulled up, creating a thin neck; 'Shoulder' shows the neck thickening into a wider section. On the right, a photograph shows the actual experimental setup, a vertical furnace with a seed crystal suspended inside.

(More information on crystal growth at <http://www.memc.com/co-as-description-crystal-growth.asp>  
Also, see animations of <http://www.memc.com/co-as-process-animation.asp>) (Photo courtesy of Ruth Carranza.)

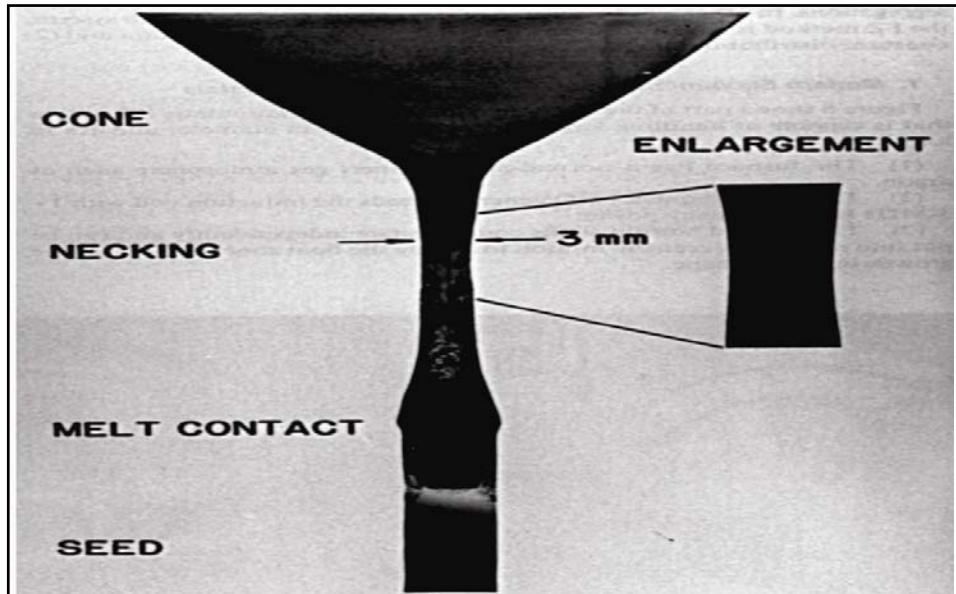
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A time-lapse sequence of eight images showing the growth of a crystal boule. The sequence starts with a seed crystal being lowered into a melt. As the seed is pulled up, a thin neck of crystal forms. The neck then thickens, forming a 'shoulder' section. The process continues as the boule grows longer and thicker.

**Figure 2.13** Time lapse sequence of boule being pulled from the melt in a Czochralski growth (reprinted with permission of Lattice Press).

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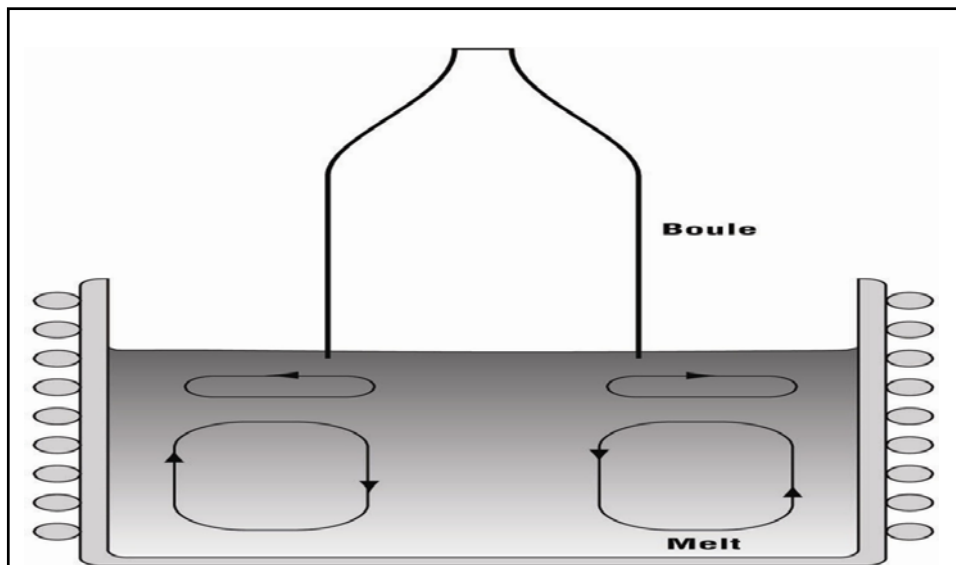
**Figure 2.15** X-ray topograph of seed neck showing edge terminated dislocations (reprinted by permission, Academic Press).

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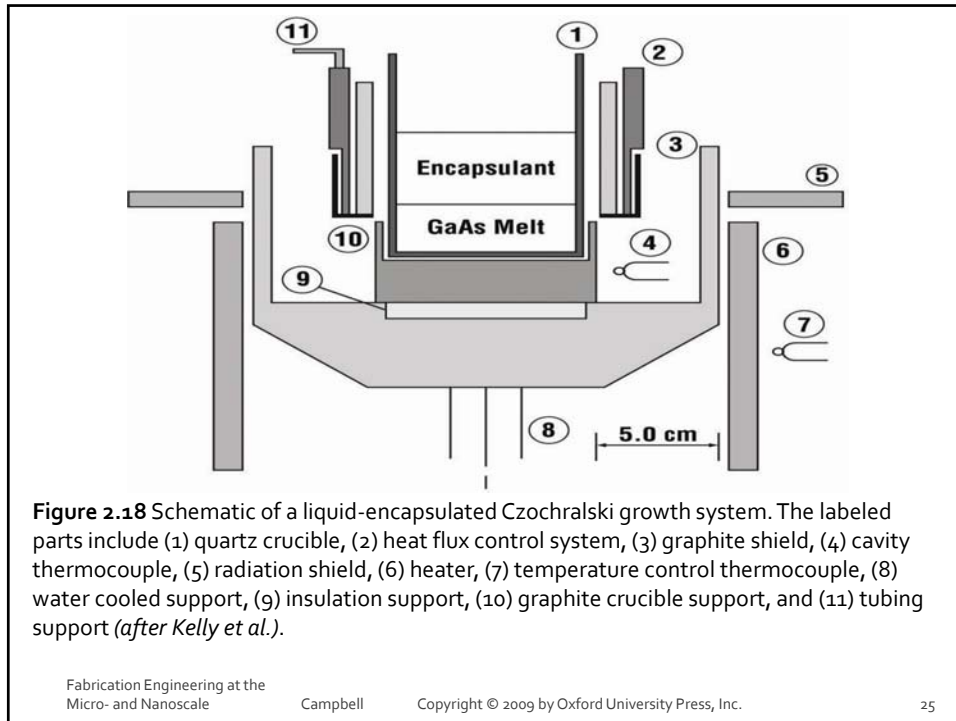
**Figure 2.17** Idealized schematization of the formation of recirculation cells in a melt.

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Polysilicon Ingot  
RF Coil  
Single Crystal Si

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

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

(See animations of crystal polishing etc. at <http://www.memc.com/co-as-process-animation.asp>)

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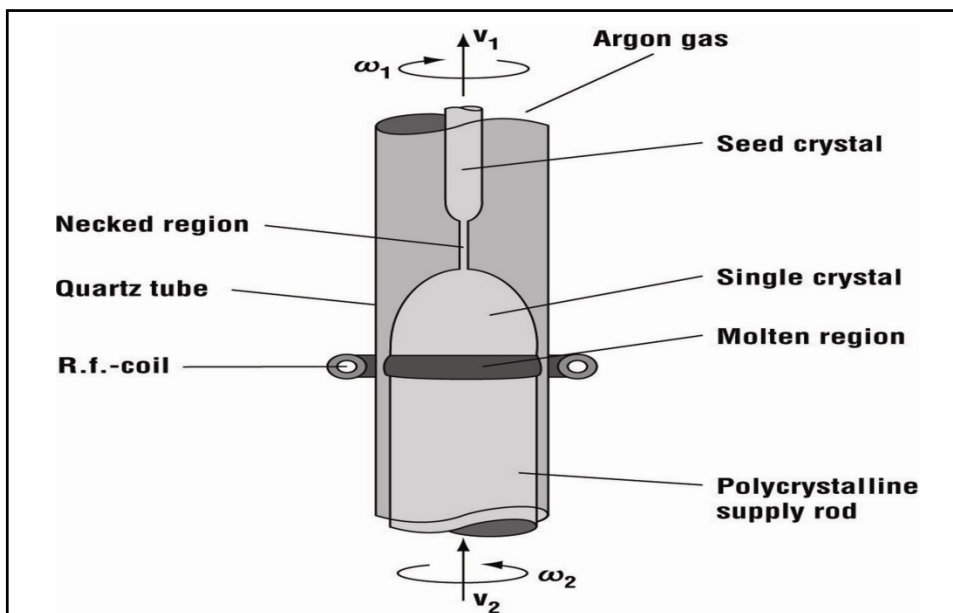


Figure 2.21 Schematic of a float zone refining system.

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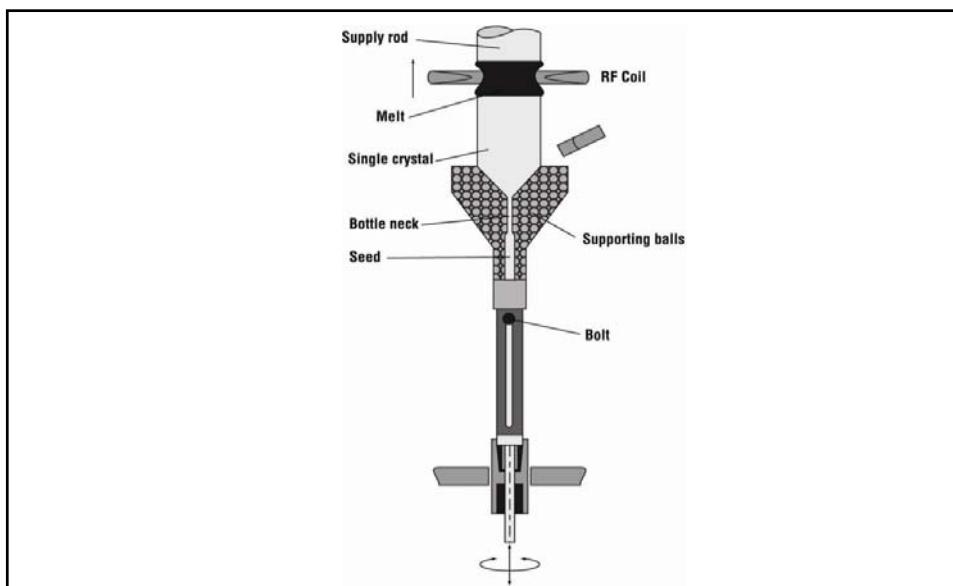


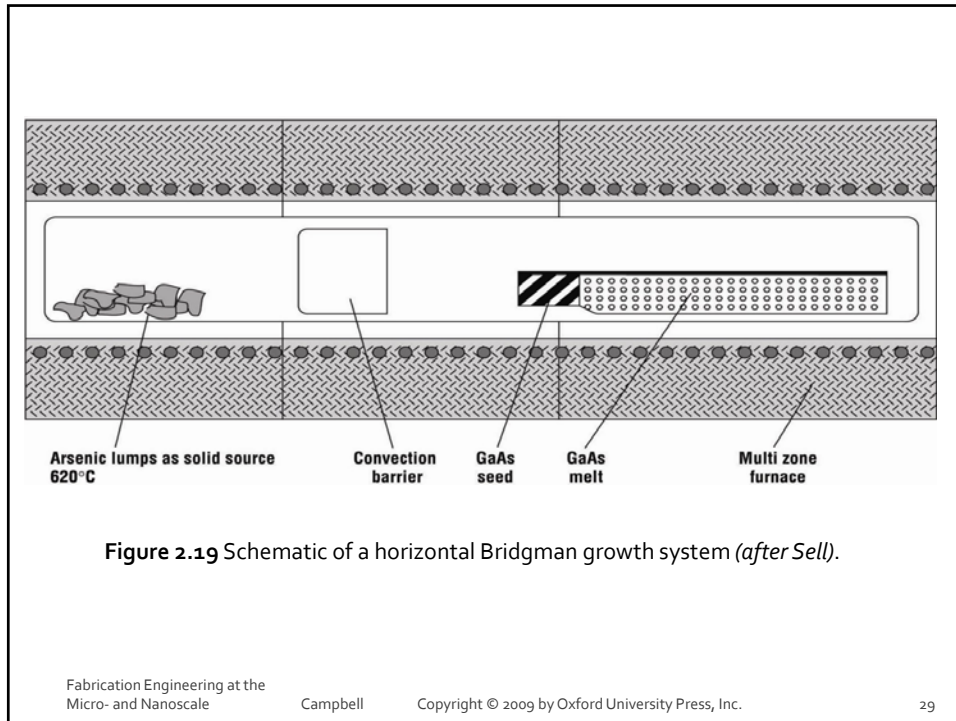
Figure 2.22 Schematic of a float zone system for growing large diameter boules (reprinted from Keller and Mühlbauer by courtesy of Marcel Dekker).

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### 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.

$L$  = 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  $x_2$

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

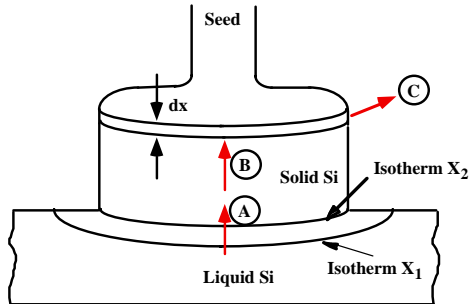
(Campbell Eqn. 2.10)

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- The rate of growth of the crystal is  $\frac{dm}{dt} = v_p AN$  (2)

where  $v_p$  is the pull rate and  $N$  is the density.

- Neglecting the middle term in Eqn. (1) we have:  $v_{PMAX} = \frac{k_s}{LN} \frac{dT}{dx_2}$  (3)  
(Campbell equation 2.11)
- 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

$$dQ = (2\pi r dx) (\sigma \epsilon T^4) \quad (4)$$

- Heat conduction up the crystal is given by

$$Q = k_s (\pi r^2) \frac{dT}{dx} \quad (5)$$

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- Differentiating (5), we have  $\frac{dQ}{dx} = k_s (\pi r^2) \frac{d^2T}{dx^2} + (\pi r^2) \frac{dT}{dx} \frac{dk_s}{dx} \cong k_s (\pi r^2) \frac{d^2T}{dx^2}$  (6)

- Substituting (6) into (4), we have  $\frac{d^2T}{dx^2} - \frac{2\sigma\epsilon}{k_s r} T^4 = 0$  (7)

- $k_s$  varies roughly as  $1/T$ , so if  $k_M$  is the thermal conductivity at the melting point,  $k_s = k_M \frac{T_M}{T}$  (8)

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

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

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

- This gives a max pull rate of  $\approx 24 \text{ cm hr}^{-1}$  for a 6" crystal (see text). Actual values are  $\approx 2X$  less than this.

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### 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.

Dopant	$k_0$
As	0.3
Bi	$7 \times 10^{-4}$
C	0.07
Li	$10^{-2}$
O	0.5
P	0.35
Sb	0.023
Al	$2.8 \times 10^{-3}$
Ga	$8 \times 10^{-3}$
B	0.8
Au	$2.5 \times 10^{-5}$

Segregation coefficient:

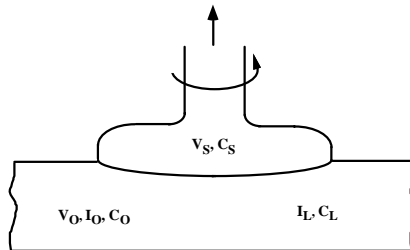
$$k_0 = \frac{C_S}{C_L} \quad (11)$$

(Campbell Eqn. 2.12)

- 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.

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



$$dI = -k_0 C_L dV = -k_0 \frac{I_L}{V_O - V_S} dV \quad (12)$$

$$\therefore \int_{I_0}^{I_L} \frac{dI}{I_L} = -k_0 \int_0^{V_S} \frac{dV}{V_O - V_S} \quad (13)$$

$$\therefore I_L = I_0 \left( 1 - \frac{V_S}{V_O} \right)^{k_0} \quad (14)$$

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

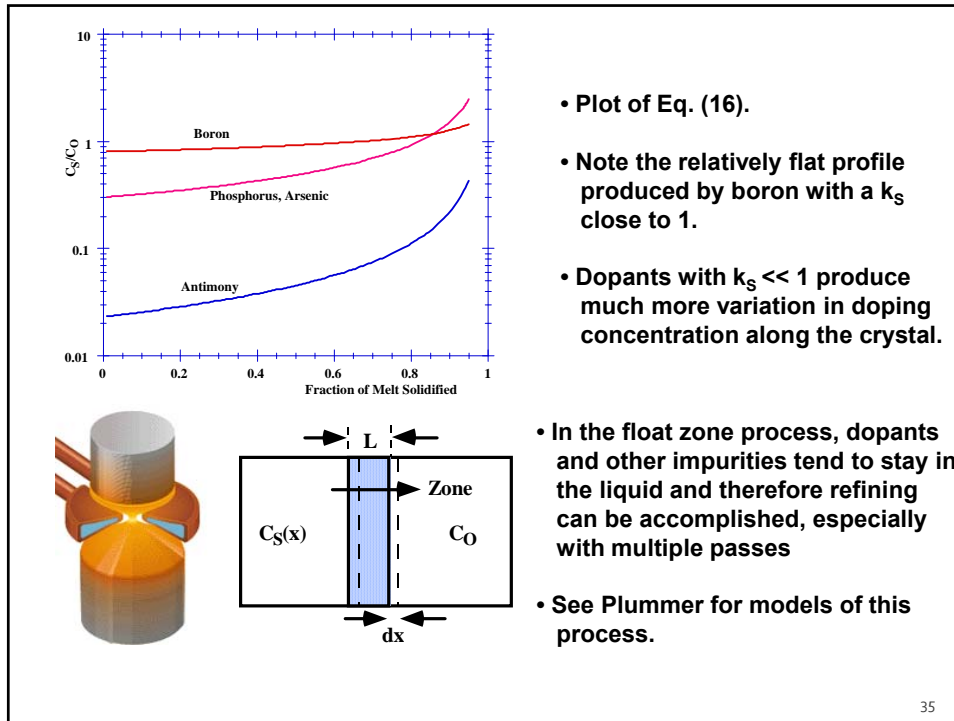
$$C_S = -\frac{dI_L}{dV_S} \quad (15)$$

$$\therefore C_S = C_0 k_0 (1-f)^{k_0-1} \quad (16)$$

where  $f$  is the fraction of the melt frozen.

(Campbell Eqn. 2.13)

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## Impurity Doping: Rapid Stirring Approx

(Solute Concentration uniform in melt)

Initially: weight of melt =  $W_m$

solute conc'n in melt =  $C_m$  ( by weight)

After time t: Crystal weight grown =  $W$

solute conc'n in crystal =  $C_s$

solute conc'n in melt =  $C_L$

weight of solute in melt =  $S$

(Freeze an element of crystal, weight  $dW$ )

Solute loses  $C_s dW = -dS$  and  $C_L = S/(W_m - W)$

Therefore:

$$\begin{aligned} dS/S &= - (C_s / C_L) (dW / (W_m - W)) \\ &= - k (dW / (W_m - W)) \end{aligned}$$

$$\int_{C_m W_m}^S dS/S = -k \int_0^W dW / (W_m - W)$$

$$\ln S \Big|_{C_m W_m}^S = -k \left[ - \ln (W_m - W) \right]_0^W$$

$$\ln S / C_m W_m = \ln [ (W_m - W) / W_m ]^k$$

Therefore:

$$S = C_m W_m [1 - (W / W_m)]^k$$

But  $S = (W_m - W) C_L$  by definition

$$= W_m (1 - W / W_m) C_s / k$$

$$= W_m (1 - W / W_m)^k C_m$$

Therefore:

$$C_s = k C_m (1 - W / W_m)^{k-1}$$

$$C_s = k C_m / (1 - W / W_m)^{1-k}$$

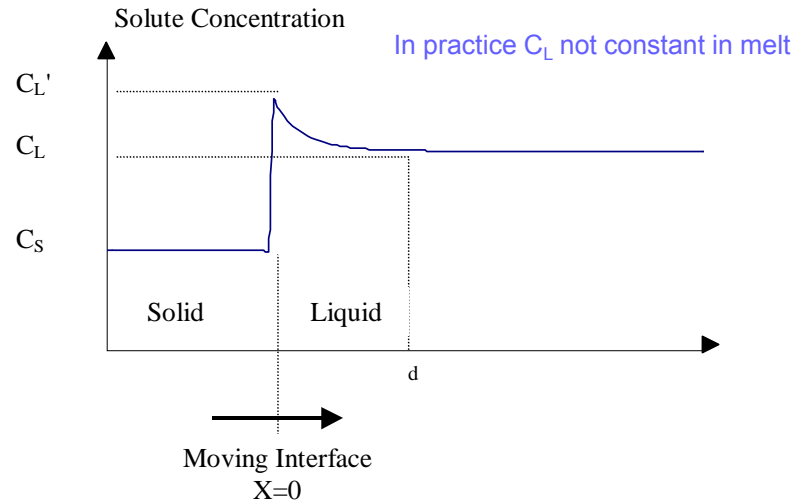
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## Impurity Doping: Partial Stirring Approx #1



## Impurity Doping: Partial Stirring Approx #2

Define  $R$  = crystal growth rate

Define  $D$  = diffusion constant of solute atoms

(typ:  $5 \times 10^{-5}$  cm<sup>2</sup>/s in liquid)

Diffusion equation at any point  $x$

$$D (d^2c/dx^2) = dc/dt \text{ \& \ } (dc/dx \cdot dx/dt) = R(dc/dx)$$

Therefore:  $D (d^2c / dx^2) = R (dc/dx)$

Solution:  $C = A \exp - (R / D)x + B$

Boundary Conditions:

1.  $C(0) = C_L' \therefore A + B = C_L'$

2. Zero net flux at  $x=0$  (neglected diffusion in solid)

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

Diffusion away from interface into liquid

Rate of rejection of solute at interface

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

$$\therefore A = (C_L' - C_S) \therefore B = C_S$$

and  $C(x) = C_S + (C_L' - C_S) \exp - (R/D) x$   
(for  $0 < x < \delta$ )

$$\therefore C(\delta) = C_L \rightarrow [(C_L - C_S) / (C_L' - C_S)] = \exp - R\delta/D$$

If we define an effective  $k_e = C_S/C_L$  and the true  $k = C_S/C_L'$

then  $(C_S / k_e - C_S) / (C_S / k - C_S) = \exp - R\delta/D$

i.e.  $k_e = k / [k + (1-k) \exp -R\delta/D]$  (Campbell 2.14)

and  $C_S = k_e C_m (1 - W / W_m)^{k_e - 1}$

In practice:  $k_e \gg k$

$k_e \rightarrow k$  if  $R\delta/D$  is large

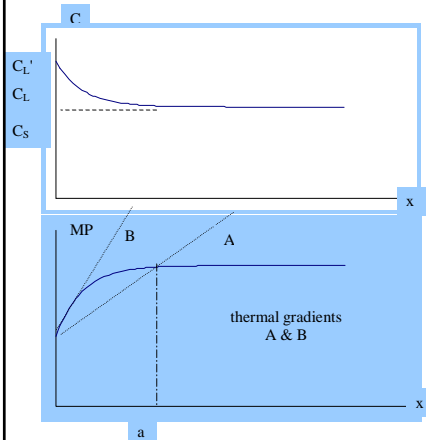
i.e. for high pull rate ( $R$  large, limits diameter)

and for low spin rate ( $\propto \delta^{-1}$ )

$$\delta = 1.8 D^{1/3} R^{1/6} \square^{-1/2} \text{ (from Sze)}$$

Can vary  $R$ ,  $\square$  to compensate for  $C$

# Supercooling



If heat flow by conduction,  
thermal gradient approx. linear  
High pull rate --> line A:  
For  $0 < x < a$ , liquid is supercooled  
i.e. get random polycrystalline nucleation  
Low pull rate --> line B:  
solidifies at surface

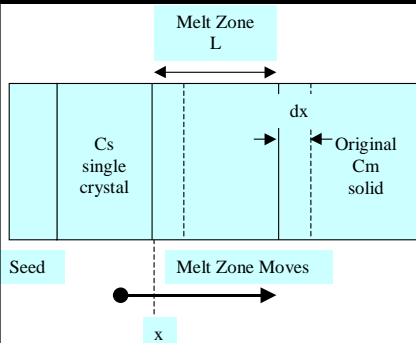
Liquid MP decreases with concentration increase  
Therefore  $MP(x)$  follows exponential  $C(x)$

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# Zone refining

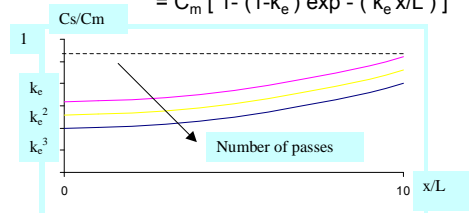


$S$  = total weight solute in zone  
 $A$  =  $c/s$  area,  $\rho$  = specific gravity  
As zone moves  $dx$ :-  
Solute added (melting end: right) =  $C_m \rho (A dx)$   
Solute lost (freezing end: left) =  $k_e S (dx/L)$

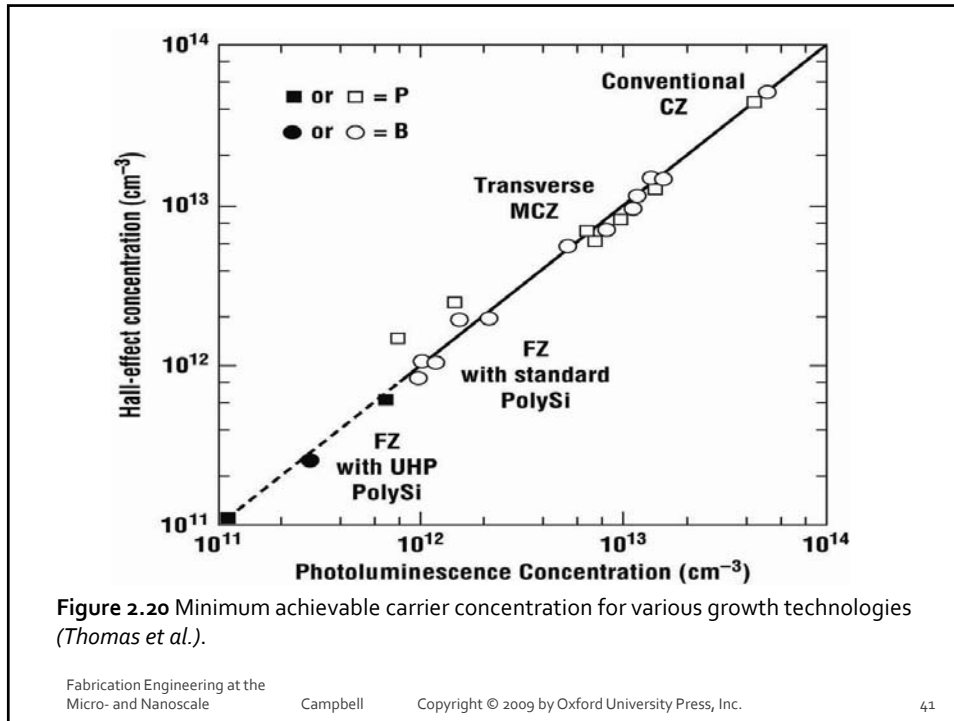
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$$\begin{aligned} \therefore dS &= C_m A \rho dx - (k_e S/L) dx \\ dS/dx &= C_m A \rho - k_e S/L \\ dS / (C_m A \rho - k_e S/L) &= dx \\ (L/k_e) \ln (C_m A \rho - k_e S/L) &= x + \text{constant} \end{aligned}$$

Evaluate constant from  $S(0) = C_m A \rho L$ , gives  
 $S = (C_m A \rho L / k_e) ( 1 - (1 - k_e) \exp - k_e x / L )$   
 But, melt zone concentration  $C_s = k_e ( S / A \rho L )$   
 $= C_m [ 1 - (1 - k_e) \exp - ( k_e x/L ) ]$



Effectively uses segregation coefficient to push impurities to one end. Then chop off!

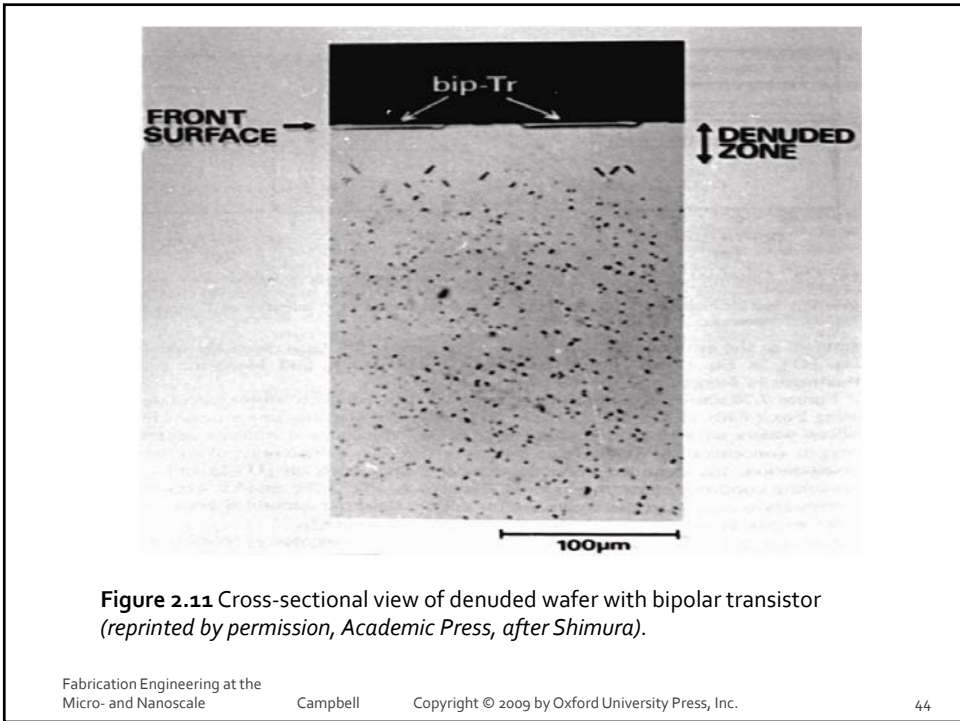
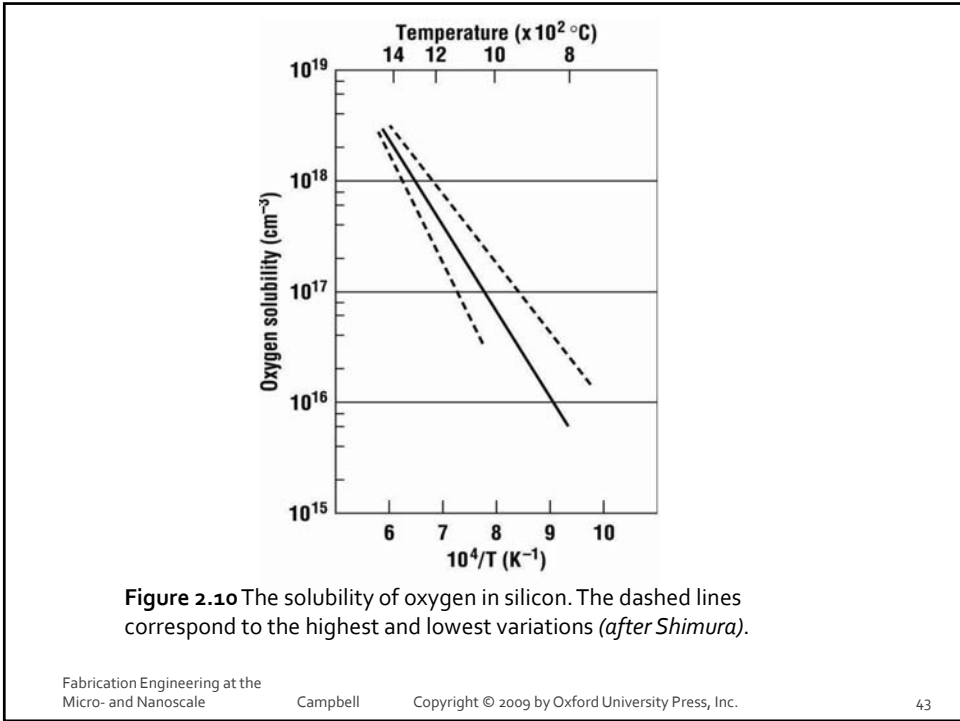


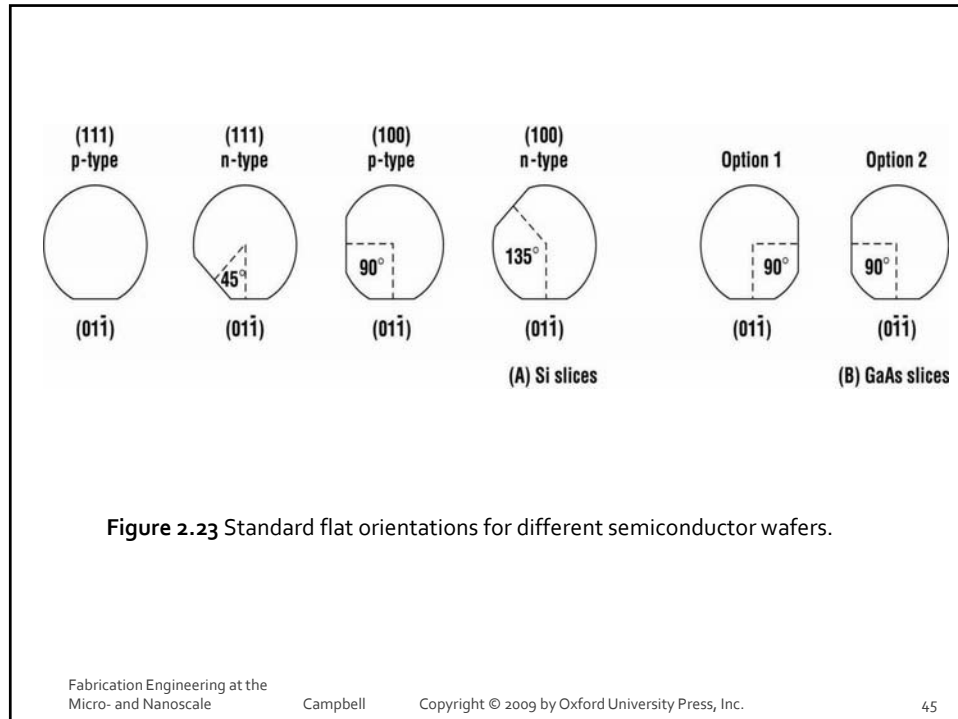
### Oxygen and Carbon in CZ Silicon

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

- O and these precipitates can actually be very useful.
- Provide mechanical strength.
- Internal gettering.

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### Summary of Key Ideas

- Raw materials ( $\text{SiO}_2$ ) are refined to produce electronic grade silicon with a purity unmatched by any other commonly available material on earth.
- CZ crystal growth produces structurally perfect Si single crystals which can then be cut into wafers and polished as the starting material for IC manufacturing.
- Starting wafers contain only dopants, O, and C in measurable quantities.
- Dopant incorporation during crystal growth is straightforward except for segregation effects which cause spatial variations in the dopant concentrations.
- Second order effects: Rapid stirring  $\rightarrow$  Partial stirring
- Point, line, and volume (1D, 2D, and 3D) defects can be present in crystals, particularly after high temperature processing.
- Point defects are "fundamental" and their concentration depends on temperature (exponentially), on doping level and on other processes like ion implantation which can create non-equilibrium transient concentrations of these defects.
- For more information see papers @ <http://www.memc.com/t-technical-papers.asp>