Crystal Growth

focus on Si + GaAs

elemental compound

Si 2-12" diameter

GaAs 2-3" typical

Si Structure

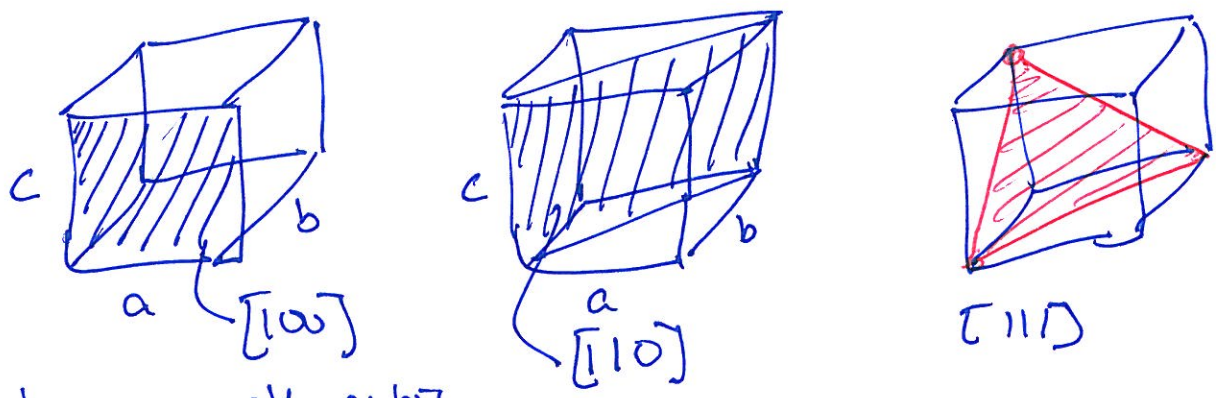
Show crystal maker model

- diamond
- tetrahedral bonding
- FCC lattice; 2 basis atoms at each lattice point → $(0,0,0)$ and $\left(\frac{a}{4}, \frac{a}{4}, \frac{a}{4}\right)$

Define directions in Crystal

Miller indices

Most common



$a = b = c$ with cubic crystals.

"Sand" Raw Mat. → Electronic Grade Si

($< 10^{13}\ cm^{-3}$ impurities)

Quartzite (pure mineral)

Carbothermal reduction

A. $SiO_2 + 3C \rightarrow \boxed{Si} + 3CO + SiO$

- 12-14 kwh kg^{-1}
- M.G.S

B. Siemens Process

Chlorination

1. $Si(s) + 3HCl(g) \xrightarrow{300°C} SiHCl_3(g) + H_2(g)$

$+ AlCl_3,\ FeCl_3,\ BCl_3$ etc.

Fractional Distillation

2. $SiHCl_3(l) \xrightarrow{32°C} SiHCl_3(g)$

3. $SiHCl_3 + H_2 \xrightarrow{CVD} 3HCl + Si(s)$

Yields E.G.S. → polycrystalline boules.

Single Crystals:
(1) Czochralski
(2) Bridgeman
(3) Float Zone.

Czochralski process

→ Show ppt figure from Sze.

→ Most wafers grown this way!
(PV etc)

Process:

→ Si Melt
→ insert oriented Si seed (small neck to reduce dislocations)

→ pull slowly and rotate

Control over impurities (ie doping)

n vs p vs p+ vs n+

growing from melt, $C_s \neq C_l$

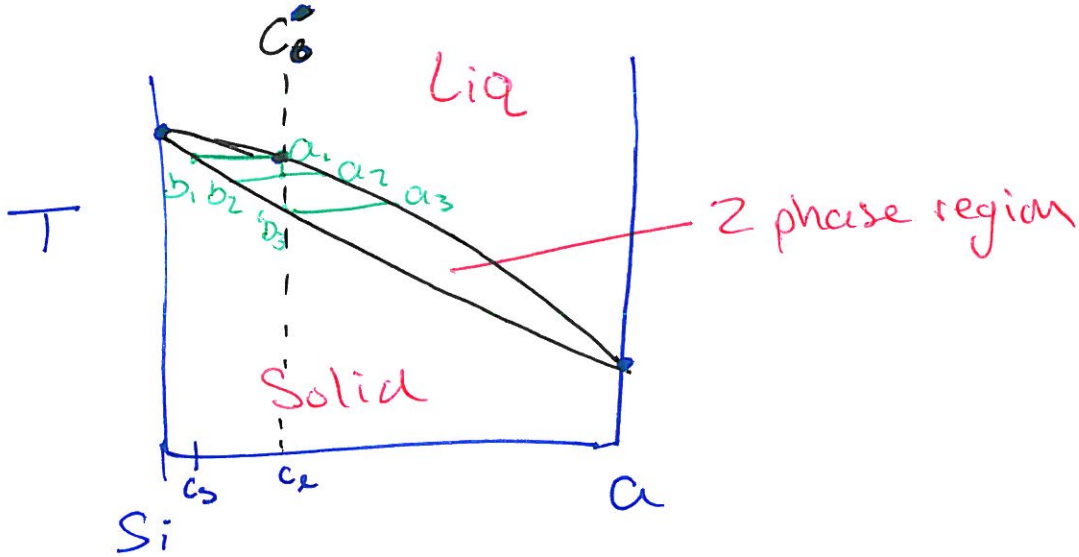
[impurity]

Solid Liquid

$K_o = C_s / C_l$ $B = 0.8$, $P = 0.35$, $Fe = 8 \times 10^{-6}$

why?

2.4 Related to Phase Diagram (expanded for Education purpose)



Composition of liquid changes when cooling takes place!

Normal Freezing Relation

Initial Melt Mass = M_0

Initial Impurity / Doping concentration = C_0

at time t: crystal weight = M

Amount of remaining Doping = S

$$\text{(1)} \quad -dS = C_s \, dM$$

change in total remaining dopant

dopant in solid grown.

(2) weight of liquid left = $M_0 - M$

↑ initial mass of liquid

$$C_\ell = \frac{S}{M_0 - M}$$ (doping in the liquid)

(1) + (2) $$\frac{-\partial S}{S} = \frac{C_s}{C_\ell} \cdot \left(\frac{\partial M}{M_0 - M}\right) = k_0 \left(\frac{\partial M}{M_0 - M}\right)$$

$$\int_{S_0 = C_0 M_0}^{S} \frac{\partial S}{S} = k_0 \int_0^M \frac{\partial M}{M_0 - M}$$

Solve via integration to get.

$$\boxed{C_s = k_0 C_0 \left(1 - \frac{M}{M_0}\right)^{k_0 - 1}}$$

Concentration of dopant depends on how much crystal has been grown!

Show plot of Normal Freezing in ppt.

Optional: work out integral → skip → just evaluating integral, etc.

$$\int_{C_0 M_0}^{S} \frac{ds}{s} = \ln(s)\Big|_{C_0 M_0}^{S} = \ln(S) - \ln(C_0 M_0) = \ln\left(\frac{S}{C_0 M_0}\right)$$

$$\int_0^M \frac{-dM}{M_0 - M} = \int_0^M \frac{dM}{M - M_0} = \ln(M - M_0)\Big|_0^M \left[= \ln\left(\frac{C_e(M_0 - M)}{C_0 M_0}\right)\right.$$

$$u = -(M_0 - M) = M - M_0$$

$$du = 1\,dM$$

$$dM = du$$

$$= \ln(M - M_0) - \ln -M_0$$

$$= \ln \frac{M - M_0}{-M_0}$$

$$\rightarrow \boxed{k_0 \ln \frac{M - M_0}{-M_0}}$$

$$\rightarrow \ln\left(\frac{C_e(M_0 - M)}{C_0 M_0}\right) = \ln\left(\frac{M - M_0}{-M_0}\right)^{k_0}$$

$$= \ln\left(\left(\frac{M - M_0}{-M_0}\right)^{k_0}\right)$$

$$\frac{C_e(M_0 - M)}{C_0 M_0} = \frac{M - M_0}{-M_0}^{k_0}$$

$$\frac{C_s}{k_0}\frac{(M_0 - M)}{C_0 M_0} = \left(\frac{M_0 - M}{M_0}\right)^{k_0}$$

$$C_s / C_e = k_0$$

$$C_s = k_0 C_0 \cdot \frac{\left(\frac{M_0 - M}{M_0}\right)^{k}}{\frac{M_0 - M}{M_0}}$$

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

$$C_s = k_0 C_0 \left(\frac{M_0 - M}{M_0}\right)^{k-1} = \boxed{k_0 C_0 \left(1 - \frac{M}{M_0}\right)^{k_0 - 1}}$$

2.5 → extra derivation

C7-

Example: want Si w/ 10^{16} B.

what is C_o

if $M_o = 60$ kg how many grams Si should be added?

Ans. $k_o = 0.8$ for Boron

$$C_\ell = \frac{C_s}{k_o} = \frac{10^{16}}{0.8} = \boxed{1.25 \times 10^{16}\ cm^{-3}}$$

Volume of Si is:

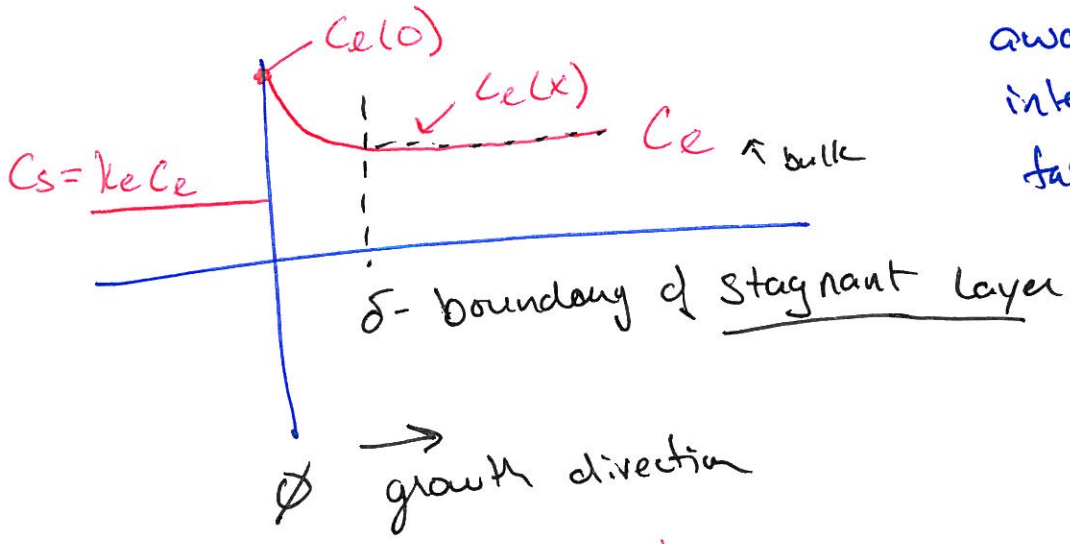
$$60\ kg\ Si \cdot \frac{1000\ g}{kg} \cdot \frac{1\ cm^3}{2.33\ g\ Si} = 2.57 \times 10^4\ cm^3\ Si$$

$$1.25 \times 10^{16}\ B\ cm^{-3} \times 2.57 \times 10^4\ cm^3 = 2.96 \times 10^{20}\ B\ atoms$$

$$\frac{2.96 \times 10^{20}\ Atoms}{6.02 \times 10^{23}\ \frac{Atoms}{mol}} \left(10.8\ \frac{g\ B}{mol}\right) = \boxed{5.3 \times 10^{-3}\ g\ B}$$

Tiny!

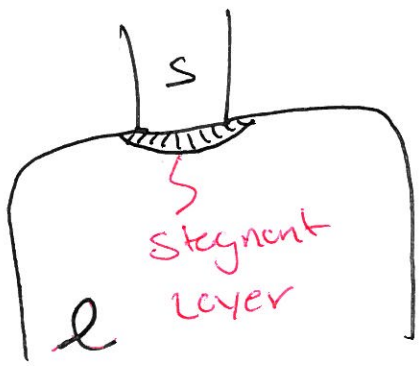
Effective Segregation Coefficient — dopants can't get away from interface fast enough



$$k_e \equiv C_s / C_e$$

crystal value

bulk value



(1) at steady-state continuity says

$$0 = v\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2}$$

C = concentration in liquid

xtal growth velocity

impurity diffusion coefficient

$\frac{\partial x}{\partial t} \cdot \frac{\partial C}{\partial x} = \boxed{\frac{\partial C}{\partial t}}$

how fast material leaves due to growth.

$D\frac{\partial^2 C}{\partial x^2} = \boxed{\frac{\partial C}{\partial t}}$

flux due to diffusion

impurity diffuse (away) due to gradient!

Solution to dif eq:

$$C = A_1 e^{-vx/D} + A_2$$

Boundary Conditions:

Stagnant Layer model.

$$C = C_\ell(0) \text{ at } x=0 \qquad C(\delta) = C_e$$

$$\underbrace{D\left(\frac{\partial C}{\partial x}\right)_{x=0}}_{J_{diff.}} + \underbrace{\left[C_\ell(0) - C_s\right]V}_{\text{flux of impurities out of growing crystal}} = 0$$

Fick's First law:

Sum of dopant flux must be zero at the interface.

Skip math... (on next page if needed) or HW!

$$e^{-v\delta/D} = \frac{C_e - C_s}{C_\ell(0) - C_s}$$

define $K_e = \frac{C_s}{C_e}$ and K_0 is $C_s / C_\ell(0)$

so $$K_e = \frac{K_0}{K_0 + (1-K_0)e^{-v\delta/D}}$$

Extra: Solve dif. Equation w/ Boundary condition

$C(x) = C_e(0)$ at $x = \emptyset$

so $C(x) = A_1 e^{-Vx/D} + A_2$

$C_e(0) = A_1 \underbrace{e^{-V(\emptyset)/D}}_{=1} + A_2 = \boxed{A_1 + A_2}$ (1)

$$\frac{\partial C}{\partial x} = \frac{-V}{D} A_1 \underbrace{e^{-Vx/D}}_{x=0 \Rightarrow 1} = \frac{-V}{D} A_1$$

so $D\left(\frac{\partial C}{\partial x}\right)_{x=0} + [C_e(0) - C_s]V = \emptyset$ (2)

$$-VA_1 + [C_e(0) - C_s]V = \emptyset$$

$$\equiv \boxed{\begin{aligned} A_1 &= C_e(0) - C_s \\ A_2 &= C_s \end{aligned}}$$ from (1)

Solution then becomes: $C(x) = [C_e(0) - C_s]e^{-Vx/D} + C_s$

now based boundary stagnant layer model $C(\delta) = C_e$

so $C(\delta) = C_e = (C_e(0) - C_s)e^{-V\delta/D} + C_s$

$$\boxed{\frac{C_e - C_s}{C_e(0) - C_s} = e^{-V\delta/D}}$$

extra

$\boxed{2.8.1}$

we also defin $K_e \equiv C_s / C_e$ and $K_o = C_s / C_e(0)$

effective K, segregation coefficient

$$\frac{K_o}{K_e} = \frac{\cancel{C_s}/C_e(0)}{\cancel{C_s}/C_e} = \frac{C_e}{C_e(0)}$$

$$e^{-V\delta/D} = \frac{C_e - C_s}{C_e(0) - C_s} \qquad K_o C_e(0) = C_s$$

$$= \frac{C_e - C_s}{C_e(0) - K_o C_e(0)} = \frac{C_e - C_s}{C_e(0)(1-K_o)}$$

$$(1-K_o)\, e^{-V\delta/D} = \frac{C_e - C_s}{C_e D} = \frac{C_e}{C_e D} - K_o = \frac{K_o}{K_e} - K_o$$

$$\boxed{\frac{K_o}{K_o + (1-K_o)e^{-V\delta/D}} = K_e}$$

which is the result in the book.

extra

2.8.2

for $v\delta/D \to \infty$, $k_e \to 1$

mak v and δ large to get uniform doping!

How? δ is $\propto \frac{1}{\text{rotation Rate}}$

→ Rotate slow? leads to slow/poor mixing and radial dependence on doping.

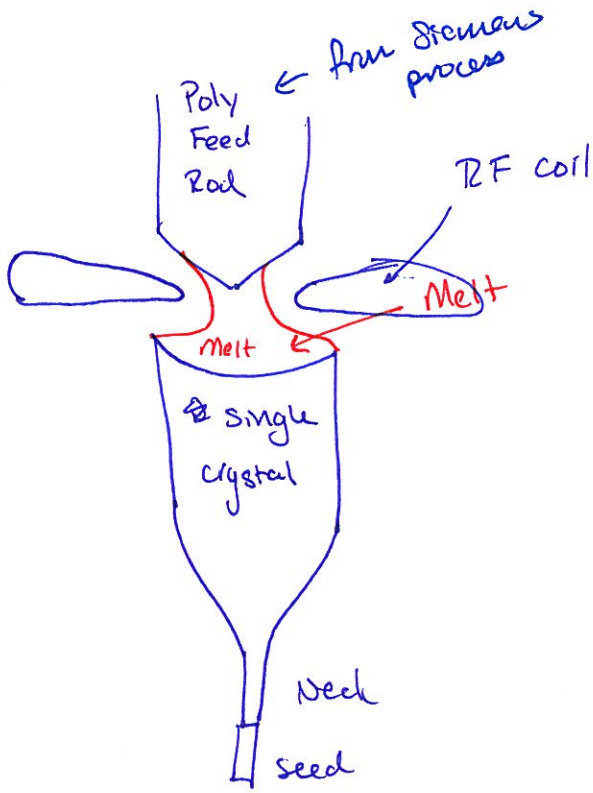
v large = pull faster.

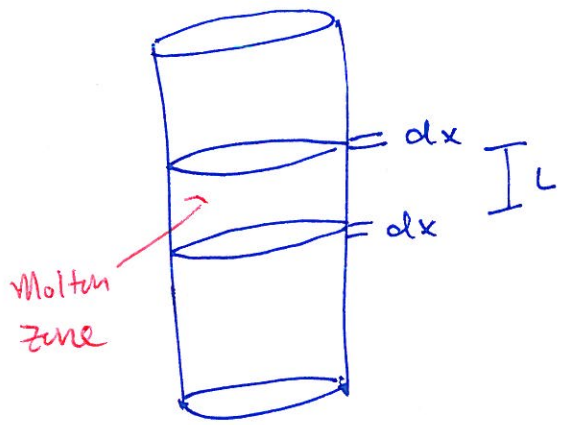
limit → must "dump" heat of crystallization somewhere

Rate of heat loss becomes limiting

Float-Zone Single Crystal Silicon

- second major method to grow Si single crystals.
- ultra high purity → no contamination from the ~~water~~ crucible
- ~~[illegible]~~ FZ Si costs more than ~~[illegible]~~ CZ





$C_o \equiv$ initial uniform doping in the rod

$L \equiv$ length of the molten zone at distance x

$\rho_{Si} \equiv$ density of Si

$S =$ amount of dopant in molten zone

As the zone moves, the amount of dopant added is $C_o \rho_d \underbrace{A\,dx}_{\text{new melted volume}}$ (1)

rod doping (in kg^{-1}) inconsistent w/ previous?

dopant removed: $= k_e \left(S \frac{dx}{L} \right)$ (2)

fraction of molten zone solidified

effective segregation coefficient.

total dopant in molten zone

so $dS = \left[\underset{(1)}{C_o \rho_d A} - \underset{(2)}{\frac{k_e S}{L}} \right] dx$

change in total dopant in molten zone

function of x

Integrate:

$$\int_0^x dx = \int_{S_0}^{S} \frac{dS}{C_0 \rho_{si} A - \frac{k_e S}{L}}$$

where $S_0 = C_0 \rho_s A L$

total dopant in the zone to start.

skip if needed...

use substitution rule

$$C_0 \rho_s A - \frac{k_e S}{L} = V$$

$$dV = \frac{-k_e}{L} dS$$

$$dS = \frac{-L}{k_e} dV$$

so,

$$x = \int_{S_0}^{S} \frac{1}{V} \frac{-L}{k_e} dV$$

$$x = \frac{-L}{k_e} \ln\left(C_0 \rho_s A - \frac{k_e S}{L}\right)\Big|_{S_0}^{S}$$

$$x = \frac{-L}{k_e} \ln\left(\frac{C_0 \rho_s A - k_e S/L}{C_0 \rho_s A - k_e S_0/L}\right)$$

$$\exp\left(\frac{-k_e x}{L}\right) = \frac{C_0 \rho A - k_e S/L}{C_0 \rho A - k_e S_0/L}$$

solve for S:

$$\left(C_0 \rho A - k_e S_0/L\right) \exp(-k_e x/L) = C_0 \rho A - k_e S/L$$

$$S = \frac{-L}{k_e}\left[\left(\boxed{C_0 \rho A} - k_e \boxed{S_0/L}\right) \exp(-k_e x/L - C_0 \rho A\right]$$

$= 2$

$$S = \frac{L\, C_0 \rho_s A}{k_e}\left[1 - (1 - k_e) e^{-L/x k_e}\right] \quad (1)$$

$$C_s = K_e\left(\frac{S}{A\rho L}\right) \quad (2)$$

dopant in growing (at retreating end) Si

dopants per unit weight in the Si ie C_e

so:

$$C_s = C_o\left[1-(1-k_e)\,e^{-k_e x/L}\right]$$

other terms cancel between (1) and (2)

key: for $k_e < 1$, C_s is $< C_o$!

impurities are "pushed" down the crystal by the molten zone.

Basis for "Zone Refining"

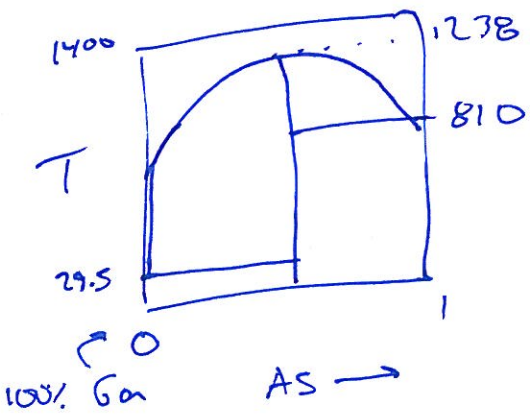
→ make several passes to push impurities out in each step.

Show graph on ppt

GaAs Crystal Growth

Binary → complicated phase diagram and melting behavior

Show pot figure



at 1238°C GaAs binary melts. <u>But high P_{As}</u>.

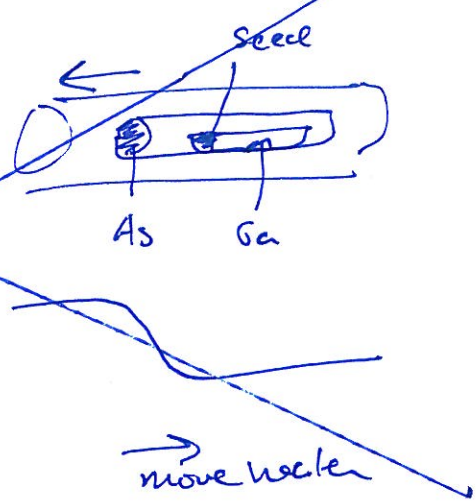
Must use L.E.C.

1cm B_2O_3 molten salt used to encapsulate crystal and prevent evaporation of As.

~~Liquid Phase Epitaxy~~

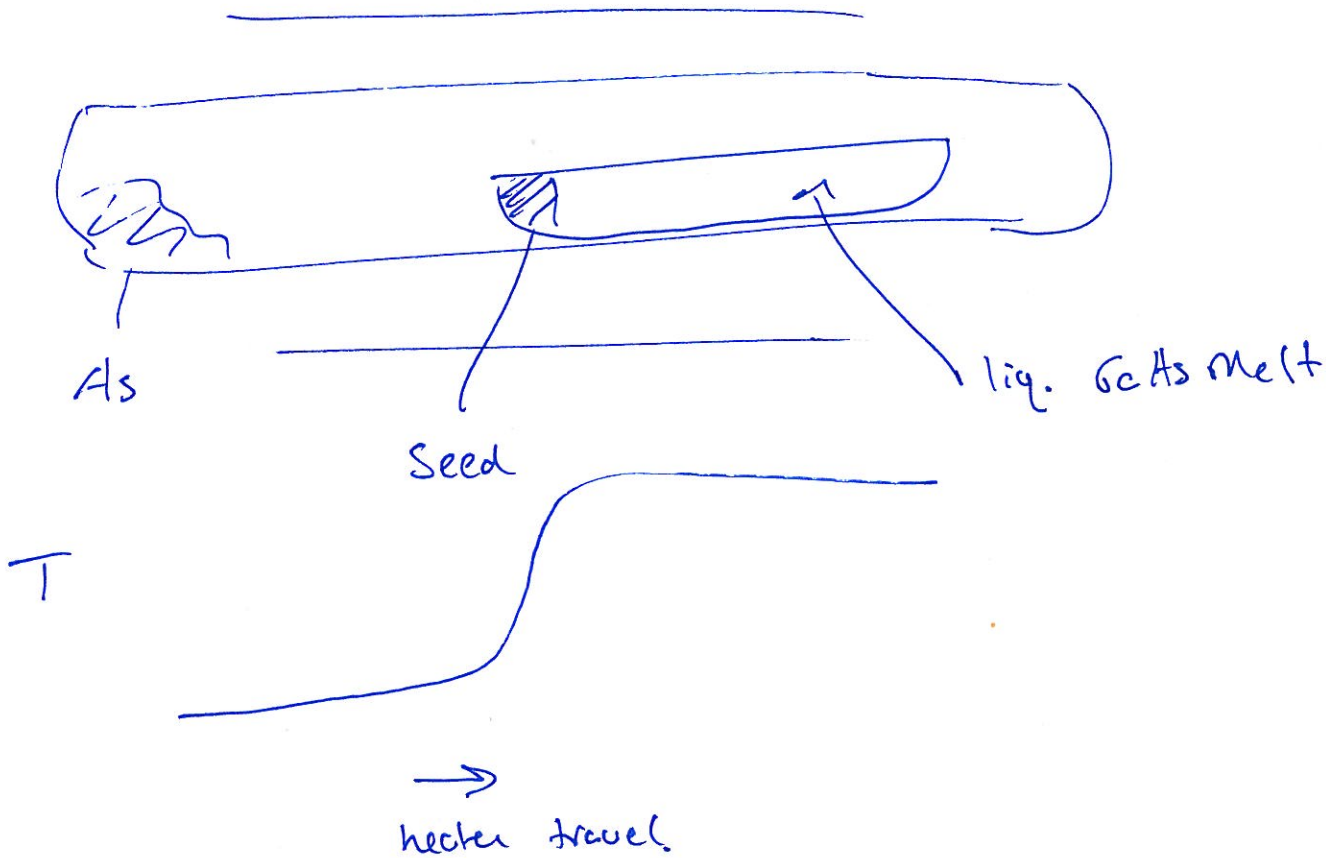
Bridgman Technique

~~xxx~~ high



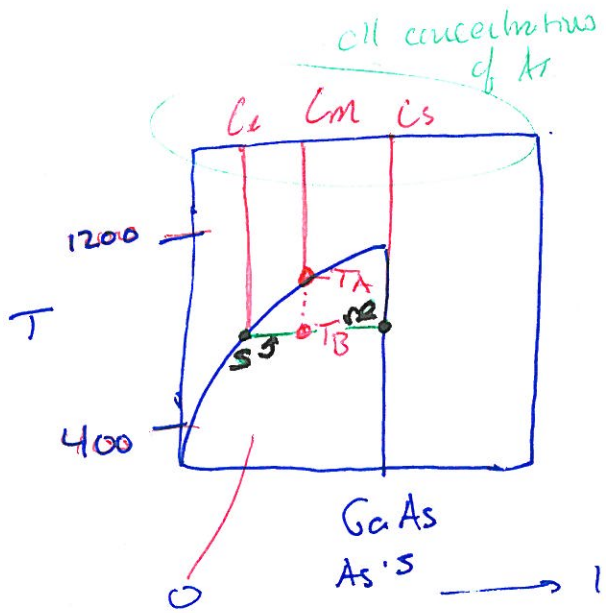
Bridgeman Technique – Show Graphic in ppt

- use sealed ampule and provide As over pressure. Heater moves to translate cold zone.



Liquid Phase Epitaxy

– show diagram of graphite boat system.



2 phase region GaAs + liquid.

Initial composition C_m at T_A

Cool to T_B

form: liquid mass: M_l
composition: C_l

Solid GaAs, mass M_s

$$M_l C_l + M_s C_s = (M_l + M_s) C_m$$

mass As in liq. — mass As in solid — initial

$$M_l C_l + M_s C_s - M_l C_m - M_s C_m = 0$$

$$M_l (C_l - C_m) + M_s (C_s - C_m) = 0$$

$$M_s (C_s - C_m) = M_l (C_m - C_l)$$

$$\frac{M_s}{M_l} = \frac{C_m - C_l}{C_s - C_m} = \frac{s}{l}$$

(move toward liquidus & section there gets longer!)

Lever rule!