

3.46 PHOTONIC MATERIALS AND DEVICES

Lecture 12: Crystal Growth

Lecture

Notes

Compound Semiconductor Crystal Growth

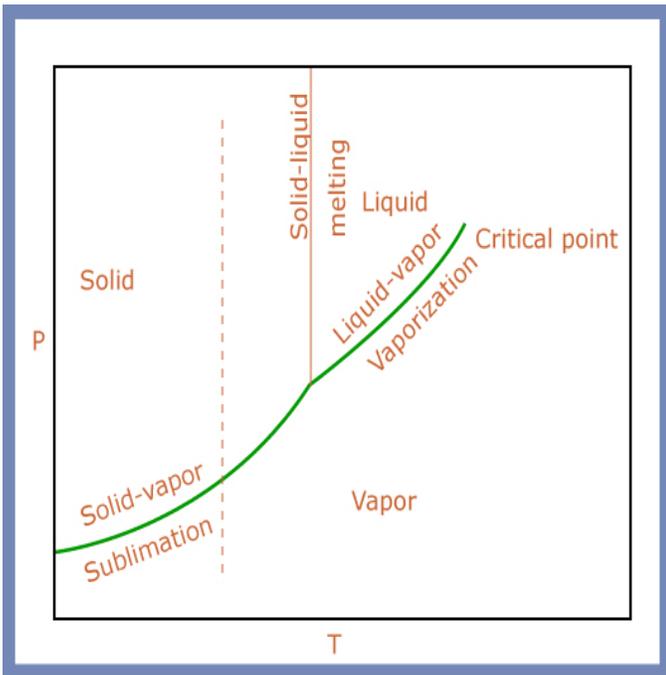
Intensive Variables

P, T, μ

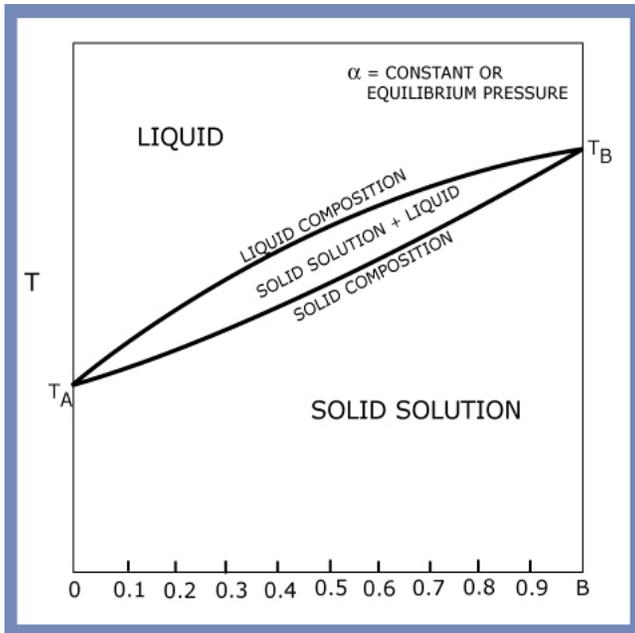
Gibbs Phase Rule

$$V = C - P + 2$$

One Component System



Two Component System

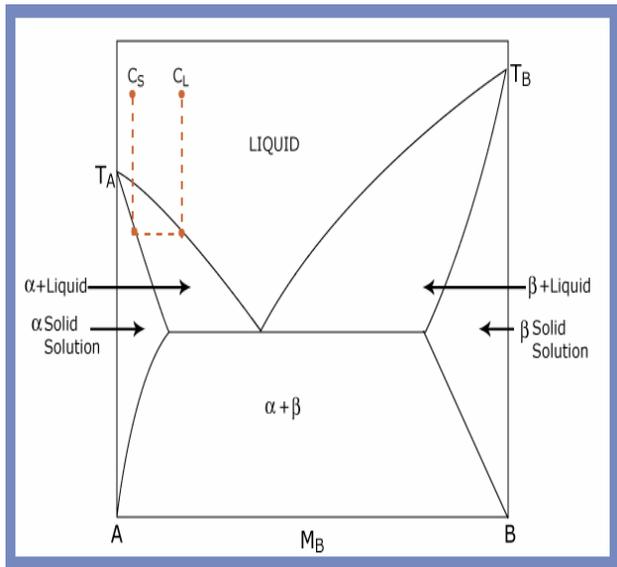


Solidification Crystalline State

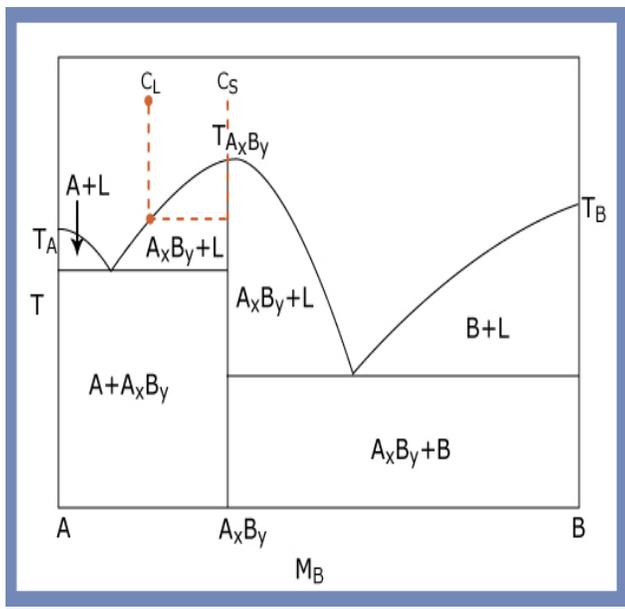
- 1) First order phase transition
 $\Delta G = \Delta U + PV - T\Delta S$
- 2) Composition C_s is richer in B than the liquid C_L .
- 3) ΔH_f latent heat of fusion is evolved.
- 4) Composition of solid varies continuously

Immiscible Systems

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



Compound formation



Crystal Growth from the Melt

Requirements:

- 1) melts congruently
- 2) does not decompose before melting
- 3) no phase transition between T_{MP} and RT.

Methods:

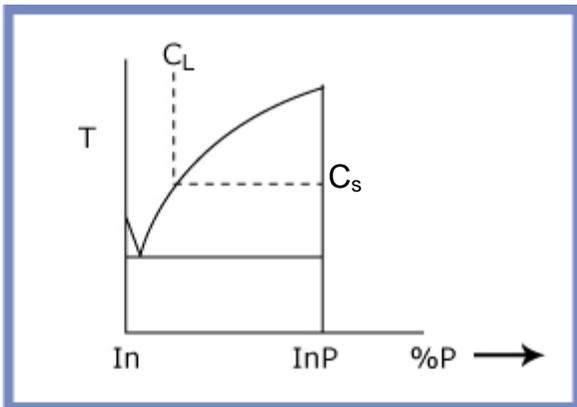
Czochralski growth

- seed
- melt with crucible
- heat flow (ΔH_f)

Gradient freeze

- boat with melt
- traveling ∇T

Solution Growth



- 1) Diffusion of solute to S/L interface
- 2) Attachment of solute atom to crystal
- 3) Evolution of ΔH_f

Vapor Phase Growth

Molecule Beam Epitaxy

MBE

Chemical Vapor Deposition

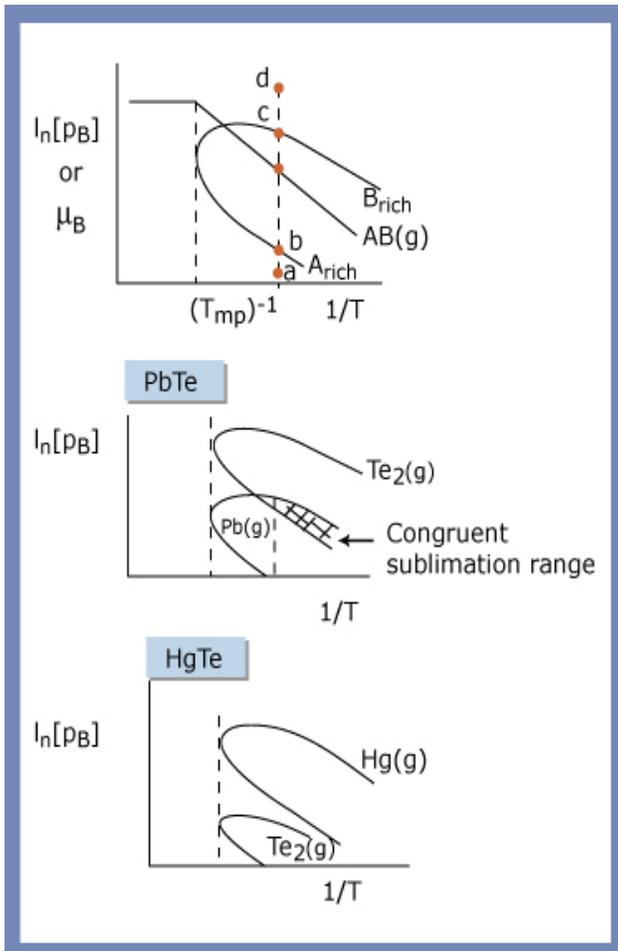
CVD

Metal Organic Chemical Vapor Deposition

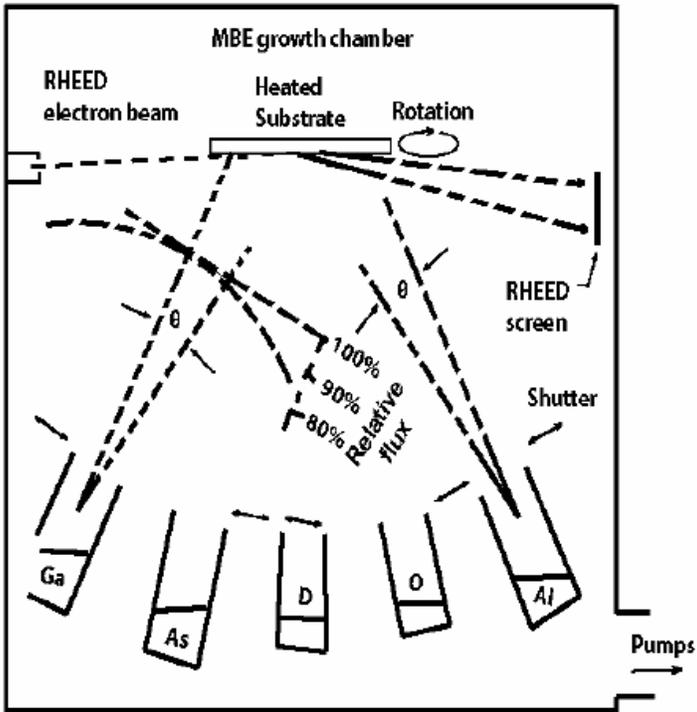
MOCVD

Vapor Phase Growth:

Gas Phase Equilibrium for AB compounds



MBE Growth



- UHV $10^{-9} - 10^{-12}$ torr
- **molecular flow** MFP \gg chamber size

$$\text{MFP} = \lambda = \left(\sqrt{2} \pi N d^2 \right)^{-1}$$

\swarrow molecule $\quad \searrow$ molecule diameter
 cm^2

$$\lambda_{300\text{ K}} \simeq \frac{0.05 \text{ torr} \cdot \text{mm}}{P}$$

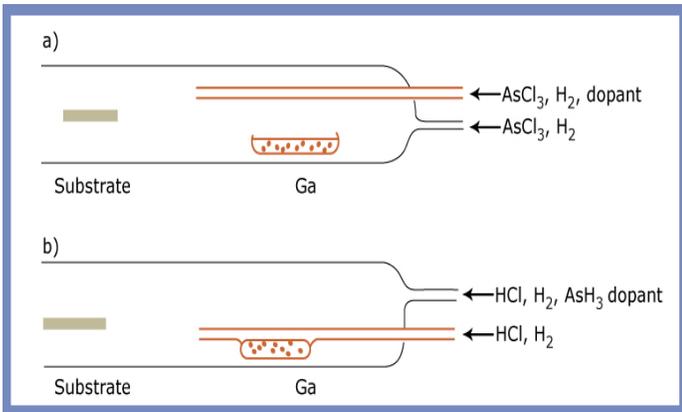
$$10^{-3} \text{ T} \Rightarrow \lambda = 50 \text{ mm}$$

$$760 \text{ T} = 1 \text{ atm} \Rightarrow \lambda = 70 \text{ nm}$$

$$[P] \propto \exp\left[-\frac{E}{kT}\right]$$

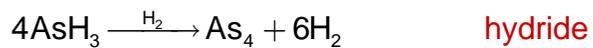
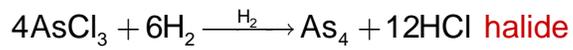
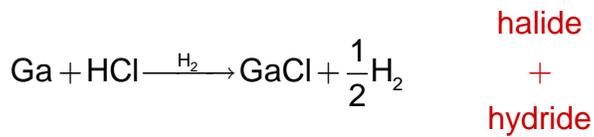
$$\phi \propto P(MT)^{-\frac{1}{2}}$$

CVD Growth

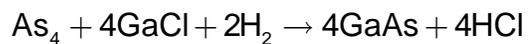


- mass transport + source reaction
- gas phase diffusion
- homogenous gas phase reactions
- heterogeneous reaction at substrate

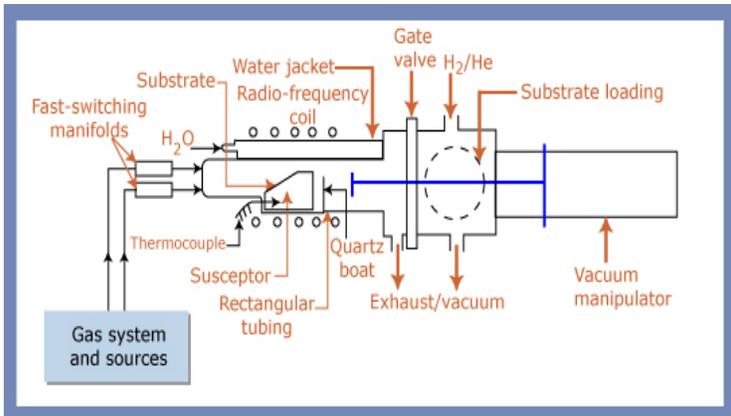
Source + transport



Deposition

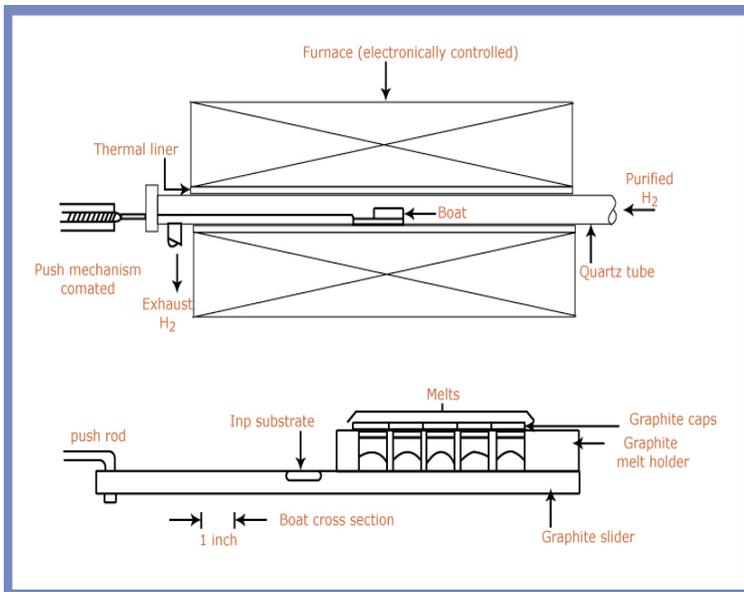


MOCVD Growth



- no source or transport reactions
 - chemistry controlled by pyrolysis of $(\text{CH}_3)_3\text{Ga}$ adsorbed on substrate
- $$(\text{CH}_3)_3\text{Ga} + \text{AsH}_3 \xrightarrow{\text{H}_2} \text{GaAs} + 3\text{CH}_4$$

LPE Growth



- In-rich side of phase diagram
- Lower $T \Rightarrow$ super saturation
- Quartz reactor, H_2 (reduces slag)
- Solid composition determined by melt composition + T