Compound Semiconductor Crystal Growth

Intensive Variables

\[ P, T, \mu \]

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) \( \Delta H_f \) 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:
Czochrakski growth
- seed
- melt with crucible
- heat flow ($\Delta H_f$)

Gradient freeze
- boat with melt
- traveling $\nabla T$

Solution Growth

1) Diffusion of solute to S/L interface
2) Attachment of solute atom to crystal
3) Evolution of $\Delta H_f$

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 \(\text{MFP} \gg \text{chamber size}\)

\[
\text{MFP} = \lambda = \left(\frac{\sqrt{2\pi} N d^2}{T}\right)^{-1}
\]

\[
\frac{\text{molecule}}{\text{cm}^2}
\]

\[
\lambda_{300\,K} \approx \frac{0.05 \text{ torr} \cdot \text{mm}}{P}
\]

\(10^{-3} T \Rightarrow \lambda = 50 \text{ mm}\)
\(760 \text{ T} = 1 \text{ atm} \Rightarrow \lambda = 70 \text{ nm}\)

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

\[
\phi \propto P(MT)^{\frac{1}{2}}
\]
CVD Growth

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

Source + transport

\[
\begin{align*}
\text{Ga} + \text{HCl} & \xrightarrow{\text{halide}} \text{GaCl} + \frac{1}{2} \text{H}_2 + \text{halide} \\
4\text{AsCl}_3 + 6\text{H}_2 & \xrightarrow{\text{halide}} 4\text{As}_4 + 12\text{HCl} \\
4\text{AsH}_3 & \xrightarrow{\text{hydride}} 4\text{As}_4 + 6\text{H}_2
\end{align*}
\]

Deposition

\[
\text{As}_4 + 4\text{GaCl} + 2\text{H}_2 \rightarrow 4\text{GaAs} + 4\text{HCl}
\]
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, \(\text{H}_2\) (reduces slag)
- Solid composition determined by melt composition + T