CRYSTAL GROWTH

1. Reactants in molten form
2. Transport to S/L interface
3. Adsorption: entropy decreases
4. Critical nucleus size
5. Growth
6. Impurities, defects more stable at high $T$; how grow pure crystal?
7. Segregation solid vs. liquid

What do we need to know prior to crystal growth?

---

Defects and crystal growth

- Defects
  - impurities, vacancies, dislocations... $T$ dependence

- Crystal growth techniques:
  - float zone, Bridgman, Czochralski

- Segregation during growth
  - Segregation coefficients
Thermodynamics and phase diagrams

6.12J / 3.155J Microelectronic processing

\[ H_B - H_A = \Delta H = \text{heat of formation of } B \text{ from } A \]

Do all reactions that give off heat proceed?

\[ S_B - S_A = \Delta S = \text{Entropy (disorder) change from } A \text{ to } B \]

Do all reactions that increase disorder proceed?

**Answer in** Gibbs free energy:

\[ G = H - TS \]
\[ G_B - G_A = \Delta G = \Delta H - T\Delta S \]

\( G \) must decrease if reaction is to proceed.
(From equilibrium, all changes increase \( G \)).

\[ \Delta H = \text{of } B \text{ from } A \]

Exothermic:

Do all exothermal reactions proceed?

\[ \Delta S = \text{from } A \text{ to } B \]

\[ \Delta G = \Delta H - T\Delta S \]

Examples:

- Exothermic: Freezing of water
- Endothermic: Melting of copper

\[ \Delta S < 0 \]

B more ordered

\[ \Delta S > 0 \]

B more disordered

Does disorder always increase in reactions?

Will not go above \( T = \Delta H / \Delta S \)

Will not go below \( T = \Delta H / \Delta S \)
Under what conditions will Si melt crystallize?

For solidification:

\[ \Delta S = S(T_{\text{final}}) - S(T_{\text{initial}}) < 0 \]

\[ \Delta H = H(T_{\text{final}}) - H(T_{\text{initial}}) < 0 \]

\[ \Delta G = \Delta H - T \Delta S \]

\[ < 0 \quad > 0 \]

\( T \Delta S \) must have smaller magnitude than \( \Delta H \)

for solidification;

this defines solidification temp.

Note the relatively large solid solubility of As in Si

...then decreases on approaching \( T_{\text{melt}} \)

Arsenic solubility in Si increases with \( T \)

Whereas this field is As + SiAs₂
1-dimensional defects: We saw soluble impurities in Si.

1-dimensional defects: More point defects

Strain field of vacancy... interstitial

Strain and surface energy can be reduced by agglomeration:
Vacancy => void,
Interstitial => precipitate

...when concentration > equilibrium
Bonding-antibonding orbital energy separation

bonding/antibonding $\Rightarrow$ energy gaps in semiconductors, insulators

\[ E \]

\[ s^2p^2 \]

\[ s^2p^3 \]

\[ s^2p^3 \]

Vacancy concentration: Vacancy requires breaking 4 bonds

Vacancy concentration:

\[ n_{\text{vac}} = n_0 \exp\left[-\frac{E_g}{k_B T}\right] \]

Empirical:

\[ n_{\text{vac}} = 5 \times 10^{22} \exp\left[-2.6 \text{ eV} / k_B T\right] \]

Equilibrium vacancy concentration:

At RT:

\[ n_{\text{vac}} = 3.4 \times 10^{-23} / \text{cm}^3 \] (\( \approx 300 \text{ km between vacancies} \))

At 1273 K:

\[ n_{\text{vac}} = 2.6 \times 10^{12} / \text{cm}^3 \] (\( \approx 700 \text{ nm between vacancies} \))

Vacancies abundant at high temperature

Arrhenius plot

\[ \ln\left(\frac{n_{\text{vac}}}{n_0}\right) = -E_a / k_B T \]

\[ \ln\left(\frac{n_{\text{vac}}}{n_0}\right) \]

\[ 1000 / k_B T \]
Oxygen impurities in Si: Observed to follow Arrhenius

\[ C_{\text{oxy}} = 2 \times 10^{22} \exp[-1.03eV/k_BT] \]

- Agglomeration => warpage, stress, dislocations
- Optimal
- No agglomeration (many isolated O²⁻ ions)

Want about 10 - 30 ppm \((7 \times 10^{17}/\text{cm}^3)\) which occurs at \(T \approx 1250^\circ\text{C}\)

Activation energies (eV):
- Oxygen: 1.03
- Eg Vacancy: 1.12
- Interstitial: 2.6
- Interstitial: 4.5

Oxygen

Anneal => denuded zone deeper than deepest feature

Dopants, impurities (substitutional, interstitial)

At RT number of intrinsic carriers:
\[ n_i = (n_e n_h)^{1/2} = n_0 \exp(-E_g/2k_BT) \Rightarrow n_i = 2 \times 10^{10}/\text{cm}^3 \]

\[ \frac{5 \times 10^{22}}{5 \times 10^{22}} \]

So doping at 1 ppm \(\Rightarrow 10^{-6} = n_{D,A}/(5 \times 10^{22}/\text{cm}^3)\)
\[ n_{D,A} = 5 \times 10^{16}/\text{cm}^3 \]

Very small doping concentration
\(\Rightarrow\) large increase in carrier concentration

What do dopants do?
\[ \sigma = \frac{ne^2\tau}{m^*} \]
\[ J = \sigma E = ne < v > \]
\[ \mu = \frac{\langle p \rangle}{E} = \frac{\sigma}{ne} = \frac{e\tau}{m^*} \]
6.152J/3.155J Microelectronic processing

CRYSTAL GROWTH

1. Confined
   Normal freezing (Bridgman)
   - horizontal crystal growth
   - vertical crystal growth

2. CZ
   Zone melting
   - Pull from solution
   - Crystal growth

3. Floating zone
   Meniscus controlled
   - Feed rod
   - High-purity crystal

- B₂O₃
- Si

Nov. 26, 2003
1) Reactants: first need high-purity Si

Making high-purity Si:

\[
\text{SiO}_2 \xrightarrow{\text{boiling}} \text{Si} + \text{CO(g)} \xrightarrow{\text{HCl}} \text{SiHCl}_3(l) + \text{H}_2 \xrightarrow{\text{distill H}_2 \text{ at } 1100^\circ\text{C}} \text{Si} + \text{HCl}
\]

MGS - 98% pure (Metallurgical grade Si)

EGS 99% pure (Electronic grade Si)
Growth rate \( \propto G_s - G_L = \Delta G \)

\[ \Delta G = 0 \Rightarrow \text{Equilibrium at} \quad \Delta H = T \Delta S, \]

\[ \Delta S = \frac{\Delta H}{T_{eq}}. \]

\[ \Delta G = \Delta H - T \Delta S \]

\[ \Delta G = \Delta H \left[ \frac{T_{eq} - T}{T_{eq}} \right] \]

Must decrease for solidification to occur

\[ \Delta H < 0 \quad \Rightarrow \quad T_{\text{interface}} < T_{eq} \]

larger (latent) heat content

\[ H_s - H_l \]

\[ \text{Crystal} \]

1) Pulling crystal from melt

At S-L interface:

\[ k_s A \frac{dT}{dz} = k_l A \frac{dT}{dz} + L \frac{dm}{dt} \]

Thermal conductivities

\[ k_s = 1.5 \text{ W}/(\text{cm} - \text{C}) \]

Heat of fusion

\[ L = 340 \text{ cal/mole} \]

If growth velocity too large, solid cannot dissipate heat (Typical \( v = 1 \text{ mm} / \text{min.} \))

\[ v_{max} = \frac{k_s}{L \rho_s \alpha_{\text{solid}}} \]

If \( T(z) \) too large \( \Rightarrow \) thermal stress
Czochralski growth of single crystals: stress, dislocations

For large temperature gradients, e.g. \( \frac{dT}{dx} \approx 100^\circ C/cm \), and given \( \alpha = 2.6 \times 10^{-6}/^\circ C \), then \( \Delta U/U = \alpha \Delta T \Rightarrow \) strains of 0.6\%, which exceeds the yield stress of Si, \( \Rightarrow \) dislocations.

Line defects: dislocations

Dislocations originate in shear strains, mostly induced by thermal gradients during growth.

A couple of dislocations/wafer is typical. Why so few?
1) “Tang” (neck at beginning of xtl) allows dislocations to move to surface.
2) Large number of atoms are involved in a dislocation, \( \Rightarrow \) high energy, \( U \)
Dislocation has low entropy (most atoms are in unique place).

\[ G = H - TS \]

is very positive
Czochralski growth of single crystals: impurities

Boundary layer keeps impurities away from solid-liquid interface

$B$ field suppresses convection of ions (reactive) deflecting them from interface

Bridgman growth of GaAs

GaAs in quartz ampule:

$dT/dx < 10^0\text{C/cm} \Rightarrow$

dislocation density $< 10^3$/cm$^2$

but melt-ampule contact $\Rightarrow$

lower resistivity.

GaAs in BN ampule:

$v \approx \text{mm/hr.}$

$\rho \approx 10 \text{M} \Omega \text{cm}$

$2 - 5 \times 10^3$ dislocations /cm$^2$
Liquid encapsulated CZ or Bridgman growth

...because vapor pressure at $T_m = 1238^\circ\text{C}$: $0.001 \times 10$ atmospheres.

B$_2$O$_3$ minimizes loss of As; $\nu \approx 1 \text{ cm/hr}$.

<table>
<thead>
<tr>
<th>$T_{\text{melt}}$</th>
<th>$\kappa$</th>
<th>Crit. resolved shear stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si 1414</td>
<td>0.21</td>
<td>1.85</td>
</tr>
<tr>
<td>Ge 960</td>
<td>0.17</td>
<td>0.70</td>
</tr>
<tr>
<td>GaAs 1238</td>
<td>0.07</td>
<td>0.4</td>
</tr>
</tbody>
</table>

GaAs cannot dissipate heat; grow slowly

GaAs cannot take stress; grow slowly

Floating zone For very high purity Si (not used for GaAs)

Top seed (molten part supported by upper crystal)

Bottom seed

seed high-purity crystal Polycrystal feed rod
Introduction of dopants via melt

Different dopants have different solubilities in solid
Define segregation coefficient, $k$, as ratio of dopant concentrations solid/melt:

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

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>As</th>
<th>B</th>
<th>O</th>
<th>P</th>
<th>Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$</td>
<td>0.002</td>
<td>0.3</td>
<td>0.8</td>
<td>0.25</td>
<td>0.35</td>
<td>0.023</td>
</tr>
</tbody>
</table>

$k < 1$ implies only a small fraction of dopant moves into solid; concentration builds up in melt as S/L interface advances...
This in turn drives up amount transferred to solid...

We can calculate the dopant/impurity concentration as a function of position in crystal (let $x =$ fraction solidified)...
Dopant or impurity concentration vs. Position

assumptions: no solid state diffusion, perfect liquid mixing

CZ growth

\[ C(x) = C_0 [L - x] \]

\[ C_s(x) = kC_0 \left[ \frac{L}{L-x} \right] \]

Float zone growth

\[ C(x) = C_0 \left[ 1 - (1-k) \exp(-kx/l_0) \right] \]

k = 0.1, l = 0.1L