Course structure
- 10 double lectures
- 2 home assignments
- 2 laboratories

Reporting
- Written report on the laboratories: SiC growth and characterization, week 49
- Problem solutions, week 49

Examination
- Written report on laboratories + problem solutions give grade 3.
- Oral presentation on a given topic + problem solution give grade 4 or 5
- Suggested dates for examination: 13/12 and 14/12

Grades
- 3, 4, 5

Course literature
  With a trial registration you can read a few chapters from the book online here.
  Here you can have some information about the book from the publishers - William Andrew and Springer.

  Information about the book from the publisher

- This book is also available as an electronic edition from Wiley InterScience Online Books:

Lecture notes will be available on the course home page
Gemstones

Photo: Mikael Syväjärvi
AlN crystal
Silicon Carbide

• The most advanced WBG semiconductor:
  • native substrates up to 3 inch on the market
ZnO bulk growth developments

- Pressurized melt growth (1-5 mm/h)
  - CERMET
  ⇒ 1 inch boules and 1cm x 1 cm oriented wafers

![X-ray θ-2θ rocking curve](image)
ZnO growth

- **Growth** => in different forms
  Virtually all growth techniques applicable

- **ZnO nanotips**: binding sites, high density, greatly enhance the immobilization of DNA

- **Nanorings**: implantable sensors for real time monitoring, e.g. blood pressure
Introduction

• The motivation and support for studying the theory and practice of crystal growth ⇒ solid state electronics
• The ever increasing application of semiconductor based electronics ⇒ an enormous demand for high quality semiconductor single crystals
• Crystal growth ⇒ multidisciplinary subject:
  ⇒ chemistry, solid state physics, theoretical physics, crystallography, thermodynamics, hydrodynamics and engineering
• The increasing demand of novel technologies for perfection, size and purity of crystals ⇒ driving force for crystal growth science
• Studies on fundamental aspects of crystallization phenomena started around 1900
• Crystal growth consists of two parts:
  ⇒ Equilibrium between crystal and the surrounding medium and the kinetics of growth
  ⇒ The first belongs to thermodynamics
  ⇒ The second considers the atomic structure of the growing surface
Introduction

- Thermodynamics (TD: T, P) helps to understand:
  - existence regions and stability behavior
  - optimal growth conditions
  - driving forces for crystallization
- TD is a phenomenological tool to demonstrate microscopic states, tendencies and directions
  - “Why...”, “When...”
- Kinetics ⇒ atomic structure and detailed steps of growth
  ⇒ “how...”, “what takes place”
Lecture 1

Elements of TD

• Crystal growth ⇒ ordered crystal structure ⇒ minimization of H ⇒ minimization of G: \( G = U + PV - TS \) ⇒ min

G- free potential of Gibbs; it is minimal if the crystal growth units (atoms, molecules) are perfectly packed in a three-dimensional ordered crystal structure, i.e. the atomic bonds are saturated regularly

U- internal crystal energy; \( U = H - PV \) ( P is pressure, V is volume)
H – enthalpy; the facto it is determined by the sum of the atomic bonds ⇒ the process of ordering is characterized by the minimization of H

• But! An ideally ordered crystalline state would imply an impossible minimal entropy \( S \). Thus the opposite process of increasing \( S \), i.e. disordering (\( S \to \max \)) gains relevance with increasing \( T \). This is expressed by the basic equation of the Gibbs thermodynamic potential ⇒ \( G = U + PV - TS = H (\downarrow) - TS(\uparrow) \) ⇒ min

• In fact, crystallization is composed of two opposite processes ⇒ (i) regular, and (ii) defective incorporation of the “growth units”, at which the second contribution increases exponentially with \( T \) and amounts at \( T=1000K \) to \( \sim 10^{-3}\% \).
Growth methods

• Crystal growth is characterized by a first order phase transition involving two contacting phases (1 and 2) separated by an interface:
  - Vapor $\Rightarrow$ Solid
  - evaporation/sublimation
  - ZnO/SiC, AlN
  - Liquid $\Rightarrow$ Solid
  - melt/solution
  - Si, GaAs/SiC

• Second order $\Rightarrow$ one phase
  - Solid $\Rightarrow$ Solid
  - polytype transformation

• Growth methods: they are based on precipitation from vapor phase and from liquid phase (melt and solution) by the knowledge of phase diagrams

• Growth techniques:
  $\Rightarrow$ Pulling (Czochralski)
  $\Rightarrow$ Zone melting (progressive melting and freezing)
  $\Rightarrow$ Progressive freezing (Bridgman)
Epitaxy

- meaning ⇒ attach in order
- process ⇒ on top of a substrate atoms are placed in an ordered fashion
- purpose ⇒ to deposit high quality films and structures
- main difference with bulk crystals growth:
  ⇒ lower temperature
  ⇒ less background impurity
  ⇒ less defects
- growth methods ⇒ from vapor and from liquid (solution)
- growth techniques:
  ⇒ MBE (GaAs, Si, ZnO)
  ⇒ CVD/MOCVD (Si, III-Vs, SiC, III-Nitrides, ZnO)
  ⇒ HVPE (GaN)
  ⇒ LPE (III-Vs, SiC, II-VI)
  ⇒ Sputtering (ZnO)
Lecture 1

Crystal growth technology to date (i)

- The world crystal production is estimated at more than 20,000 tons per year.
- The largest fraction of ~60% are semiconductor Si, GaAs, InP, GaP, CdTe and its alloys.
- Optical crystals, scintillator crystals, and acousto-optic crystals have about equal shares of 10%.
- Laser and nonlinear optic crystals and crystals for jewellery and watch industry have shares of a few % only.
It is postulated that for a specific crystal of defined size and perfection there is only one optimum and economic growth technology.

**Figure 1.5** Schematic diagram of the efficiencies of various crystal-growth methods and the achieved crystal sizes and crystal quality. Note that there is normally only one optimum economic technology for the required crystal performance and size.
Crystal growth technology to date (iii)

- Crystal growth technology is a progress determining factor in many important areas ⇒ novel high technologies, energy saving, solar energy generation, in future laser fusion energy, etc.
- Special education is needed because of the complexity of the CGT

<table>
<thead>
<tr>
<th>Table 1.1  Complexity of crystal growth technology CGT</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>a. Multi-Disciplinary</strong></td>
</tr>
<tr>
<td>• Chemistry (all fields) including Chemical Engineering</td>
</tr>
<tr>
<td>• Materials Science &amp; Engineering</td>
</tr>
<tr>
<td>• Mechanical &amp; Electrical Engineering (especially hydrodynamics, machine design, process control)</td>
</tr>
<tr>
<td>• Theoretical Physics (especially thermodynamics, non-equilibrium thermodynamics, statistical mechanics)</td>
</tr>
<tr>
<td>• Applied Crystallography and Crystal Chemistry</td>
</tr>
<tr>
<td>• Solid-State Physics</td>
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<tr>
<td><strong>b. Complexity</strong></td>
</tr>
<tr>
<td>• Phase Transformation from Fluid (melt, solution, vapour) to Crystal</td>
</tr>
<tr>
<td>• Scaling Problem: Control of surface on nm scale in growth system of ~m size, hampers numerical simulation</td>
</tr>
<tr>
<td>• Complex Structure &amp; Phenomena in Melts and Solutions</td>
</tr>
<tr>
<td>• Multi-Parameter Processes: Optimize and compromise ~10 parameters</td>
</tr>
</tbody>
</table>

There is only one Optimum and Economic Growth Technology for a Specific Size and Performance of Crystal or Crystalline Layer!
Equilibrium point-defect concentration (i)

- Considering ordering (H) and disordering (S) forces in crystal formation it is not possible to grow an absolutely perfect crystal \( \Rightarrow \) in reality “no ideal” but only an “optimal” crystalline state can be obtained \( \Rightarrow \) in thermodynamic equilibrium the crystal perfection is limited by incorporation of a given concentration of point defects \( n \) (only point defects are able to exist in an equilibrium state)

\[
\Delta G = \Delta H_d - \Delta S_d T \to \text{min}
\]

(2.2)

Neglecting any effects of volume change, defect type and defect interplay at constant pressure the equilibrium defect concentration \( n \) can be determined from the change of thermodynamic potential by introducing the defect as

with \( \Delta H_d = nE_d \) the change of internal energy at incorporation of \( n \) defects, having a defect formation energy \( E_d \), and \( \Delta S_d = k \ln(N!)/[n!(N-n)!] \) the accompanying change of entropy (configurational entropy) with \( k \) the Boltzmann constant and \( N \) the total number of possible sites. After substitution and application of Stirling’s approximation for multiparticle systems like a crystal \( \ln N! \approx N \ln N, \ln n! \approx n \ln n \), \( \ln(N-n)! \approx (N-n) \ln(N-n) \) Equation (2.2) becomes

\[
\Delta G = nE_d - kT[N \ln N - n \ln n - (N-n) \ln(N-n)]
\]

(2.3)

Setting the 1st derivation of Equation (2.3) \( \partial \Delta G/\partial n = 0 \), which equals the energetical minimum defect concentration \( n_{\text{min}} \), and considering \( N \gg n \) the ‘perfection limit’ of a crystal is

\[
n_{\text{min}} = N \exp(-E_d/kT)
\]

(2.4)

exponentially increasing with temperature.

Using \( N \approx N_A \) (Avogadro’s constant) = \( 6 \times 10^{23} \) mol\(^{-1} \) and \( E_d = 1 \) eV (vacancy formation energy in copper, for example) the minimum defect concentrations \( n_{\text{min}} \) at 1000 K and 300 K are about \( 6 \times 10^{18} \) mol\(^{-1} \) and \( 10^7 \) mol\(^{-1} \), respectively.
Equilibrium point-defect concentration (ii)

Figure 2.1  Schematic illustration of the equilibrium defect concentration (‘perfection limit’) $n_{\text{min}}$ obtained by superposition of defect enthalpy $\Delta H_d$ and entropy $\Delta S_d$ using Equations (2.2)–(2.4). (Reprinted from P. Rudolph, Theoretical and Technologica Aspects of Crystal Growth, 1998, copyright (1998) reprinted with permission from Trans Tech. Publications Ltd.)

Figures 2.1 and 2.2 show the $G(n)$ and $n(T)$ functions schematically. Due to the limitation of diffusion rate a certain fraction of high-temperature defects freezes in during the cooling-down process of as-grown crystals (broken lines) and exceeds the equilibrium concentration at room temperature markedly (Figure 2.2). In other words, in practical cases the intrinsic point-defect concentration is still far from thermodynamic equilibrium. Note, in the case of formation of vacancy-interstitial complexes (Frenkel defects) the value of $n_{\text{min}}^{(F)}$ is somewhat modified and yields $\sqrt{n_{\text{is}}N} \exp(-E_d^{(F)}/kT)$ with $n_{\text{is}}$ the total number of interstitial positions depending on the given crystal structure.
Equilibrium point-defect concentration (iii)

Figure 2.2 Minimum defect concentration vs. temperature at $E_d = 1\text{ eV}$ (1) and $2\text{ eV}$ (2) after Equation (2.4). Dashed lines: the ‘freezing in’ courses of high-temperature defects.

Hence, depending on the device requirements the technologist has to decide the necessary purification and equilibration of a given material. For instance, semiconductor laser diodes need high-doped material ($>10^{17}\text{ dopants per cm}^3$) allowing a residual point defect level of less than $10^{16}\text{ cm}^{-3}$, but semi-insulating (SI) material for high-frequency devices requires the highest possible purity. Today, the standard level of residual contaminations in SI GaAs does not exceed $10^{14}\text{ cm}^{-3}$, for example.
The phase transition (i)

- Most growth methods are carried out near equilibrium (exceptions are MBE and MOCVD) ⇒ the equilibrium state, as described by phase diagram, should serve as a useful guide to the T and P conditions.

- Two phases are in equilibrium when the Gibbs potentials of the phases \( G_1 \) and \( G_2 \) are equal ⇒ the potential difference between the phase is zero \( \Delta G = 0 \)

- For a single component (e.g. Si) and at uniform T and P, one can write:

\[
G_1 = U_1 - TS_1 + PV_1 \\
G_2 = U_2 - TS_2 + PV_2 \tag{2.5}
\]

\[
G_1 - G_2 = \Delta G = \Delta U - T \Delta S + P \Delta V = 0
\]

- The change of the internal energy ⇒ \( \Delta U = \Delta H - P \Delta V \)

- Typically, a melt-solid phase transition involves relatively small volume changes ⇒ \( \Delta V \approx 0 \).

In this case the free Helmholtz potential \( F \) can be used in the phase equilibrium.
The phase transition (ii)

Helmholtz potential

\[ \Delta F = \Delta G_{V,P=\text{const}} = \Delta H - T_e \Delta S = 0 \]  

(2.6)

with \( \Delta H \) the enthalpy released by crystallization (latent heat of fusion), \( \Delta S \) the transition (melting) entropy and \( T_e \) the equilibrium temperature (melting point). Thus, at the phase transition the enthalpy, entropy, internal energy and volume change abruptly (see Equation (2.5)) and Equation (2.6) becomes \( \Delta H = T_e \Delta S \).

Table 2.1 shows the parameter changes of selected materials at vapour–solid, liquid–solid and solid–solid phase transitions.

This is of practical relevance for crystal growth. For instance, the growth-rate-dependent liberated heat participates in the thermal balance at the melt–solid phase transition according to

\[ k_i \frac{dT_i}{dz} - k_s \frac{dT_s}{dz} = \frac{\Delta H}{c} v \]  

(2.7)

with \( k_{i,s} = \frac{\lambda_{i,s}}{(\rho_{i,s} c_{i,s})} \) the thermal diffusivity (\( \lambda \) – heat conductivity, \( \rho \) – density, \( c \) – heat capacity), \( dT_{i,s}/dz \) the temperature gradient along the growth axis \( z \) in the liquid (l) and solid (s) phase, and \( v \) the growth rate. In most cases, \( \Delta H \) is conducted away through the growing crystal. For instance, at a typical value of \( \Delta H/c \approx 10^3 \) K (silicon) a crystallization velocity of 10 cm h\(^{-1}\) releases the heat quantity \( \Delta H v/c \) (right term in Equation (2.7)) of \( 10^4 \) K cm h\(^{-1}\). Hence, a temperature gradient greater than 20 K cm\(^{-1}\) is required to conduct this heat through the growing crystal with thermal diffusivity of \( 5 \times 10^2 \) cm\(^2\)h\(^{-1}\) (no temperature gradient is assumed in the melt).
The phase transition (iii)

**Table 2.1** The abrupt change of thermodynamic parameters at first-order phase transitions of selected materials

<table>
<thead>
<tr>
<th>Phase transition (1 → 2)</th>
<th>Material</th>
<th>Volume change $(V_1 - V_2)/V = \Delta V/V$ (%)</th>
<th>Entropy change $S_1 - S_2 = \Delta S$ (J/mol K)</th>
<th>Enthalpy change $H_1 - H_2 = \Delta H$ (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>vapour–solid (v → s)</td>
<td>Al</td>
<td>$&gt; -99.9$</td>
<td>345</td>
<td>$250 \times 10^3$</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>$&gt; -99.9$</td>
<td>304</td>
<td>$304 \times 10^3$</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>$-6.0$</td>
<td>11</td>
<td>$11 \times 10^3$</td>
</tr>
<tr>
<td>liquid–solid (l → s)</td>
<td>Si</td>
<td>$+9.6$</td>
<td>30</td>
<td>$50 \times 10^3$</td>
</tr>
<tr>
<td></td>
<td>GaAs</td>
<td>$+10.7$</td>
<td>64</td>
<td>$97 \times 10^3$</td>
</tr>
<tr>
<td></td>
<td>ZnSe</td>
<td>$-19.6$</td>
<td>7</td>
<td>$13 \times 10^3$</td>
</tr>
<tr>
<td></td>
<td>LiNbO3</td>
<td>$-20.9$</td>
<td>17</td>
<td>$26 \times 10^3$</td>
</tr>
<tr>
<td>solid–solid (s₁ → s₂)</td>
<td>BaTiO₃ $\rightarrow$ C</td>
<td>0</td>
<td>0.5</td>
<td>$0.2 \times 10^3$</td>
</tr>
<tr>
<td></td>
<td>ZnSe $\rightarrow$ ZB</td>
<td>0</td>
<td>0.5</td>
<td>$1.0 \times 10^3$</td>
</tr>
<tr>
<td></td>
<td>CsCl $\rightarrow$ NaCl</td>
<td>$-4$</td>
<td>10</td>
<td>$7.5 \times 10^3$</td>
</tr>
<tr>
<td></td>
<td>C$_{GR} \rightarrow$ D</td>
<td>$-37$</td>
<td>4.8</td>
<td>$1.2 \times 10^3$</td>
</tr>
</tbody>
</table>

In the case of vapour growth the heat of vaporization is released during condensation (i.e. deposition) of the solid phase. For instance, in the layer-by-layer growth mode, assisted by a discontinuous two-dimensional nucleation mechanism, the liberated thermal impulse is $I_T (\Delta H/c) \Delta z$ with $\Delta z$ the crystallizing step width. Assuming a spacing between layers $\Delta z = 6.5 \times 10^{-8}$ cm and $\Delta H/c \approx 6 \times 10^3$ K (ZnSe at 1000°C) the heat $I_T$ of about $4 \times 10^{-4}$ K cm per layer has to dissipate through the growing crystal (i.e. substrate) and ambient.