Sub processes and control

- sublimation of the source material (source heating)
- nucleation on the seed (supersaturation and surface kinetics!)
- crystal feeding (mass transport!)
- boule growth (temperature distribution!)

• Mass transport aspect of vapor growth is most difficult to control

The phenomena involved are very complex and strongly depend on the geometry of the system

• A number of parameters to be controlled ➤ sublimation, mass transport, nucleation, Si/C ratio, uniformity of supersaturation, surface kinetics, etc.

• Growth rate $\sim \frac{\Delta T}{\Delta L \cdot P_{Ar}}$

• Diffusion limited

• Schematic representation of the processes involved in growth of SiC crystals form vapor phase
Input vs. output parameters

- Growth $T \rightarrow$ growth rate, polytype
- $T$-gradient $\rightarrow$ growth rate, crystal quality
- Pressure $\rightarrow$ growth rate, purity
- Source to seed distance $\rightarrow$ growth rate, crystal length
- Heating of the source $\rightarrow$ growth rate, growth front
- Seed type and quality $\rightarrow$ polytype, crystal quality

Schematic representation of the processes involved in growth of SiC crystals form vapor phase
- sublimation, mass transport, nucleation, crystal growth.
• The growth rate exponentially increases with growth temperature

• An apparent activation energy of the growth process can be derived from the slope

• This activation energy is consistent with the activation energy of SiC sublimation (enthalpy of sublimation 148 kcal/mole)

➤ The growth process is not limited by the sublimation of the source

Arrhenius plot of growth rate; Measurements are done at 5 mbar Ar pressure and source to seed distance 5mm.
With decreasing Ar gas pressure growth rate increases and tends to saturate below 2 mbar. Such behavior is commonly observed and it is consistent with the pressure dependence of the molecular diffusion coefficient inversely proportional within some range where molecular collisions take place. The region of pressure where the growth rate does not vary is relevant to collision free molecular transport this may be interesting for the practice, but other problems may appear, e.g. vapor composition control Growth of SiC bulk crystals is always done in diffusion limited region.

Dependence of the growth rate of SiC on the inert gas (Ar) pressure at 2450°C and source to seed distance 10 mm.
The growth rate has a linear dependence on the inverse distance in a broad temperature range 2300-2450°C. It is shown by the theory that such a dependence is true for diffusion mass transport:

\[ R \sim \frac{\Delta T}{\Delta L \cdot P_{Ar}} \]

Growth rate vs. source to seed distance for three different temperatures, at 5 mbar Ar pressure.
SiC Growth Modes

**Growth modes**

- **2D - layer growth:**
  - 2D nucleation on singular surfaces
  - Spiral growth
  - Step-flow on vicinal surfaces

- **3D growth:**
  - Island growth at higher supersaturation
  - Depends also on the surface state

**Typical growth patterns in spiral mode:** C- and Si face (from left to right)
SiC crystal structure

- Hexagonal structure (close packed)
- Two lattice constants: \( a \) and \( c \)
- Polar faces in [0001]
- Possibility of different stacking order along \( c \)-axis ➤ more than 200 polytypes
- Most important polytypes: 4H, 6H and 3C
- Vicinal surface is obtained by a small (several degrees) miscut towards [11-20]
- (11-20) plane is the most dense ➤ more kinks will be available for growth
• How to produce them?

• Schematic of a crystal with atomic layers
  • In SiC these are bilayers Si-C, because the bond between Si and C atoms is very strong
  • If the crystal is sliced perpendicularly to the c-axis obtained wafers are called on-oriented and they will not contain regular steps, they will have few steps and large terraces.
  • When the crystal is sliced under some angle in respect to the c-axis obtained wafers will contain regular steps on these vicinal surfaces (off-axis wafers)
Growth on well oriented and vicinal surfaces (i)

- Growth on singular surfaces ➤ 2D-nucleation
- Growth on vicinal surfaces ➤ step flow mode

- For SiC: if growth is performed on large terraces (singular face) cubic (3C) phase may appear and even twins are formed because two stacking orders are possible ➤ crucial for epitaxy (low temperature)
Growth of SiC on vicinal surfaces

- Growth on vicinal surfaces ➤ step flow mode and micro-step bunching

- The steps are highly regular, straight and uniformly distributed (a)
- The step height of many steps is 1.5nm, i.e. 6 times the Si-C bilayer => the unit c lattice parameter of 6H-SiC. This is related to minimization of the surface free energy during crystal growth.
- The surface energies for each SiC bilayer plane are different due to the stacking sequence of the polytype (b).
- A particular terrace with the lowest energy dominates the surface and the possible step bunching in 6H-SiC is the formation of 3 bilayer height steps (ABC or ACB layer steps in 6H-SiC).

a) AFM image from 6H-SiC (000-1)C surface
b) The possible terraces on 6H-SiC (0001)
c) The energetically favoured unit cell height step
Spiral Growth of SiC and defects

- Most common on well oriented substrates ➤ requires the lowest supersaturation

- In this mode continuous growth occurs during which screw dislocation is persistent in the middle of the spiral.
- If the dislocation in the seed crystal are many, they may interact as the growth proceeds ➤ strain energy will be accumulated and above certain value of the Burgers vector a hollow core dislocation will be formed, called micropipe.
- Micropipes can be observed in the middle of spirals, or after chemical etching (molten KOH for SiC)

Micropipe along the c-axis

In the middle of a spiral

After hot KOH etching
Commercial equipment for SiC boule growth

SB50 System for 2-inch crystal growth of SiC using sublimation

- Reactor cabinet
- Electronics cabinet
- Loading cabinet

Courtesy of Epigress
High temperature CVD growth - a comparison with PVT

Possibility of continuous supply of the source material

Inherent advantages for Si-SiC growth

- high vacuum
- high purity of the sources gases
- possibility to adjust C/Si
SiC commercial wafers

- Seeded Sublimation Growth (SSG)
  - most developed for SiC growth
  - 100mm wafers on the market
  - Growth from vapor phase more difficult to control in respect to growth rate, crystal size, and structural defects increased prime cost

4H-SiC, commercial wafer
Vapor growth of II-VI semiconductors

- II-VI => ZnSe, CdTe, ZnO, etc.
- For these materials crystallization from vapor phase by physical vapor transport (PVT) has some advantages (as compared to melt growth) => (i) lower processing temperature; (ii) purification effect as a result of the difference in the vapor pressures of the native elements and the impurities; (iii) higher interfacial morphological stability of the solid-vapor interfaces.
- In the PVT, the species found in the vapor phase => Zn or Cd (II group) and diatomic molecules of group VI elements (O\(_2\), S\(_2\), Se\(_2\), or Te\(_2\)).
- The transport rate is controlled => by the temperature of the source, the partial pressure of the species (II and VI\(_2\)) and the enclosed gas pressure.

Note*: the partial pressure of the components can vary by orders of magnitude as the composition of the compound varies over the homogeneity range => stoichiometry control important
- Sizable crystals of high quality can be obtained => e.g. ZnSe crystals 40-45 mm in diameter.

Fig. 15.9. ZnSe single crystal grown by a seeded vapor-phase free method in <100> direction and (100) substrate cut from such crystal (from Reference 66)
Free-growth method

• Markov-Davydov technique or seeded PVT (SPTV) => closed system

  • Polycrystalline source => put in a chamber with perforated walls in the upper part of the ampoule
  • A seed crystal => placed below at a definite distance on the center of a quartz or sapphire pedestal
  • The total pressure in the ampoule => 1 atm
  • H₂ or mixture with Ar => residual atmosphere in sealed ampoules;
  • Source T ~1200°C, seed T ~1165°C

Fig. 15.10. Growth ampoule and temperature profile for the growth of ZnSe crystals by a seeded vapor-phase free growth (from Reference 65)

• In a horizontal system with double seeds at the ends and source in the middle up to 2 inch diam. and 25 mm length obtained by Eagle-Picher Industries. Tsource ~1200°C and the difference with the crystal < 100°C.
The source is loaded in an ampoule, in which a vent hole of 1-2mm is made. The ampoule is placed in an outer quartz tube, which is sealed off at one end and connected to a vacuum pump and an Ar supply connected in parallel. Ar has been shown to make the leakage of the excess component from the growth zone controllable. The residual Ar pressure is adjusted to a value allowing congruent sublimation. Three zone resistance heated furnace, T is controlled in each zone by thermocouples.
• Horizontal geometry (Eagle Picher developed SPVT):
  Substrates up to 40mm in diameter demonstrated with FWHM of 40 arcsec.
  ⇒ The growth rate is very low (1mm/day)
  ⇒ The crystals suffer from non-uniformity that makes the material very expensive ($2000 per substrate).
• Vertical geometry:
  ⇒ Physical vapor transport (PVT) growth of mm-size, polycrystalline ZnO has been demonstrated at temperatures exceeding 1600°C under air at atmospheric pressure.
  => Scanning electron microscopy (SEM) analysis revealed the growth of grains and microcrystals with strong faceted morphologies suggesting near-equilibrium growth conditions.
  ⇒ Scanning electron microscopy (SEM) analysis revealed the growth of grains and microcrystals with strong faceted morphologies suggesting near-equilibrium growth conditions.
  ⇒ In addition, a temperature-dependent formula for the O₂ sticking coefficient has been developed to predict the maximum growth rate of PVT ZnO. Combining this formula with an existing one-dimensional analytical model for PVT growth of bulk AlN, the value of the growth rate of PVT ZnO as a function of temperature and oxygen vapor partial pressure has been studied.
  ⇒ This analysis predicts that growth rates in the order of 1mm/h could be theoretically achieved using the PVT method under non-stoichiometric oxygen-rich vapor pressures and temperatures exceeding 1600°C.
CVT method

- Chemical vapor transport (CVT) => iodine is widely used as the chemical agent, allows crystal growth at temperatures far below transition temperatures (melt and vapor).
- The principle => seed and source are placed at the ends of a closed quartz ampoules together with calculated amount of iodine.
  ⇒ The role of the iodine is to react with the source material (e.g. ZnSe) and to transport it to the seed, where the compound will decompose and ZnSe will be released on the seed (Iodine => transport agent)
  ⇒ Since iodine is not consumed by the crystal its amount can be calculated and related to the growth time.
  ⇒ The partial pressure of different components present inside the ZnSe-I2 system during CVT growth of ZnSe single crystals is calculated assuming mass conservation of iodine.
  ⇒ Using the partial pressure of different components inside the ampoule the optimum growth conditions for the growth of good quality ZnSe single crystals can be predicted theoretically.
  ⇒ The growth rate is very low, the process takes place for several days.
  ⇒ Essential problem is the convective transport, it has to be decreased to maintain stable growth conditions and crystal morphology.
  ⇒ The quality of the crystals is very good, but the size is rather small
**CVT grown crystals**

- Recently 1 inch in diameter ZnSe crystals => grown

Small crystal (earlier)

- Schematic illustration of the ampoules. Two types of ampoules (type 1 and type 2) are prepared. $\theta$ indicates the angle at the conical tip.
- After loading with all materials, the ampoule is evacuated to a pressure $3 \times 10^{-7}$ Torr.
- When the ampoules are heated up, the pressure will increase $\Rightarrow$ the total pressure and the sum of the partial pressures of the reaction species are important for the growth rate and the morphological stability of the crystals.
CVT growth of ZnSe

• Basic reactions:

\[ \text{ZnSe}(s) + \text{I}_2(g) = \text{ZnI}_2(g) + \frac{1}{2}\text{Se}_2(g), \]  
\[ \text{I}_2(g) = 2\text{I}(g). \]

• Effect of growth temperature

![Graph showing growth rate versus temperature](image)

- The optimum growth $T$ (seed), which enables growth of single crystals and high growth rate, is around $850^\circ C$.

Fig. 2. Dependence of growth rate and crystallinity on the growth temperature. These results are obtained using an identical ampoule. The arrows represent the order of the experiments. Solid circles (●) represent the growth of single crystal. Open circle (○) represents the growth of polycrystal.
Effect of iodine concentration

- Total pressure is considered => equivalent to the iodine concentration
- Increase of the growth rate in region C is related to convective mass transport (assuming mass transport limits the growth rate) => thermal convection prevails at high pressure.
- Generally, the convective transport causes random nucleation at the growth front resulting in twin boundaries, voids and even polycrystalline material => significant contribution of convective mass transport should be avoided in CVT of ZnSe.
- The increase of the growth rate in region A => not well explained.
- The optimum iodine concentration should be situated in region B from the view point of morphological stability and high growth rate.
- Other optimum conditions: T=>~850°C; seed orientation =>(111)B, angle of the conical tip => 30°; iodine concentration => 1.1 mg/cm³.

Fig. 4. The dependence of growth rate and morphological stability on the total pressure in the ampoule. Symbols (● ○) represent the results from run No. 5-A–D using furnace A. Symbols (● ○) represent the results from run No. 6-A–H using furnace B. Symbols (■ □) represent the results from run No. 7-A–D using furnace C. Solid symbols (● ■ ○) indicate the growth of single crystal with stable facets. Open symbols (○ □ ◊) indicate unstable growth. Solid lines show the calculated curves taking account of only diffusive mass transport.