

**Themenblock 7:
Spezielle Verfahren/Anwendungen**



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**“Crystal growing devices for
compounds semiconductors”**

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Dieser Artikel liegt nur in englischer Sprache vor.

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- Industrie- und Laboröfen
- Induktionserwärmung
- Mikrowellenerwärmung
- Probenvorbereitung für Spektroskopie
- Hochtemperatur Technologie

- Industrial- and laboratory furnaces
- Induction heating
- Microwave heating
- Sample preparation for spectroscopy
- High temperature technology



Mikrowellenkammeröfen,
MKT, bis 100 kW, 30 m³
Microwave chamber dryer,
MKT, up to 100 kW, 30 m³



Induktions-Feingußanlage, Supercast, bis 0,5
kg Mg, 1,2 kg Ti/TiAl, 2 kg Stahl
Induction centrifugal fine casting unit, Super-
cast, up to 0,5 kg Mg, 1,2 kg Ti/TiAl, 2 kg steel



Kammeröfen mit Luftumwälzung,
KK-U, bis 850 °C, 3 m³, 160 kW
Chamber furnaces with air circulation,
KK-U, up to 850 °C, 3 m³, 160 kW



Mikrowellen-Banddurchlauf-Trockner,
MDBT, bis 30 m / 150 kW
Microwave continuous belt dryer,
MDBT, up to 30 m / 150 kW

Crystal growing devices for compounds semiconductors

1 Introduction

Silicon is still the most important material of choice in semiconductor devices, but there is a increasing demand for other materials in special applications where silicon reaches its physical limits. Nowadays there is a great demand for high frequency electronics in mobile phones and optoelectronic components in communication technology. These areas are the domain of gallium arsenide (GaAs) and indium-phosphide (InP).

SiC (4H/6H) is a very promising semiconductor material for the realisation of innovative devices in high power and temperature electronics, for sensors in extreme environment and blue/UV optoelectronics and LED's for the automotive industry.

Single crystalline fiber made of oxide material becomes more and more important for telecommunication and laser applications.

Bulk crystals of silicon as a single element semiconductor are easier to grow, while the properties of GaAs and InP depend on stoichimetry of its compounds which are mainly influenced by the growth conditions.

Melt growth of pure Silicon Carbide cannot be realized due to extreme pressure and temperature.

2 Methods and Machines

2.1 Gallium arsenide and indium phosphide

The market of optoelectronic devices includes high brightness light emitting diodes and diode lasers. For example, todays conventional lamps are going to be partially replaced by light emitting diodes due to their lower consumption of energy. The same applies for lasers: There are plans to partially exchange solid state lasers for applications like welding and cutting by semiconductor lasers, or at least to use diode lasers for optical pumping of solid state lasers.

Because of the high current and power densities in the active zones of these devices, crystal defects in the substrates e.g. dislocations lead to a rapid device degradation. Therefore single crystals with a low defect density and a high homogeneity are required. In the case of gallium arsenide a typical upper bond for the dislocation density, which is measured in terms of the etch pit density (EPD), is 500 cm^{-2} . Additionally, a charge carrier density (n) of $0.8 \cdot 10^{18} - 3.0 \cdot 10^{18} \text{ cm}^{-3}$ is necessary to enable the substrate to carry current densities in the order of some kA/cm^2 .

As the standard growth technique for III/V-materials, the liquid encapsulated Czochralski (LEC) technique, is not able to provide crystals which fulfill the requirements mentioned above, a new growth technique (**V**ertical **G**radient **F**reeze, VGF) was developed within the last decade.

In the VGF-technology, the polycrystalline GaAs is molten in a boron-nitrate crucible. After the melting process the material is directionally solidified from a single-crystalline seed at the bottom of the crucible. This is achieved by lowering the temperature while maintaining a positive temperature gradient in the melt. As the crystal growth is usually performed in multi-zone furnaces there are many degrees of freedom. Numerical modelling is applied for the optimization of the furnaces and the growth processes.

At the beginning of the nineties the Chair of Electrical Engineering Materials at the University of Erlangen asked Linn High Therm to realize a new concept of a multi-zone furnace for investigation on the VGF process, with the opportunity of easy computer simulation and a maximum in degrees of freedom in the variation of the temperature field with time and place.

Table 1:

| Crystal growth conditions | Demands on crystal Growth apparatus | Technical realization | Furnace with fibre insulation | Cold wall furnace |
|---|--|---|-------------------------------|-------------------|
| Reduction of radial T-gradients | Local heat transfer (high flexibility in imposing thermal boundary conditions) | Multizone set up including active cooling | ++ | +++ |
| Stoichiometry control during growth process | Furnace construction has to be inert against aggressive gases in the case of ampoule rupture | Avoidance of porous materials (fibres, powders, granulates) for thermal and electrical insulation | - - - | +++ |
| | Easy cleaning has to be guaranteed | Modular set up of materials with dense surface | - - - | +++ |
| High inert gas pressure | High power density | Heating elements with respective surface load | +++ | +++ |
| In-situ annealing | High heating and cooling rates | Reduced thermal mass Active cooling | - - - | +++ |

Table 2:

| Thermal data | MZCW-furnace | Multizone furnace Fibre insulation |
|------------------------------------|-------------------------------|---------------------------------------|
| Working temperature (°C) | 1300 - 1350 | 1350 |
| Temp. gradient (K/cm) | >150 | = 50 |
| Heating rate (K/s) | >10 | 1.5 |
| Cooling rate (K/s) | >10 | 0.3 |
| Power consumption (kW) at 1 bar | 1.5 – 2 (T = 1100-1200 °C) | 4 (T = 1250°C) |
| Thermal flexibility | see fig. | no data available |

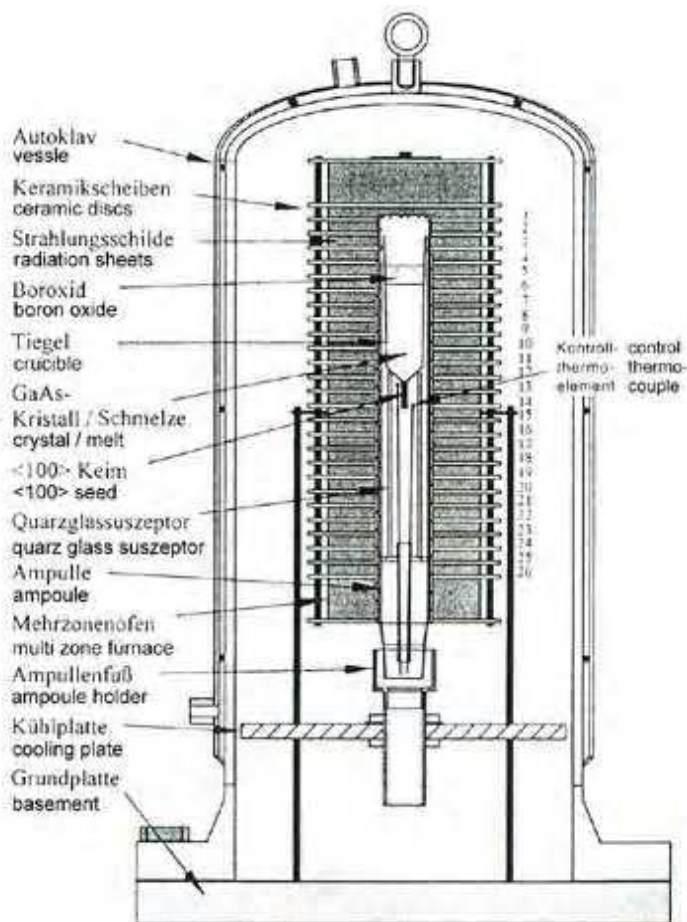


Figure 1: 26-zone crystal growing VGF-furnace

The result was a multi zone furnace in coldwall technology (MZCW) with 23 combined heating and cooling segments (length = 2 cm). Each segment is controlled independently.

This prototype allows the growth of 2-3 inch crystals up to a maximum length of about 20 cm. Due to this design the temperature gradient can be shifted by software control without mechanical moving parts. The whole construction is installed inside a 10 bar pressure vessel.

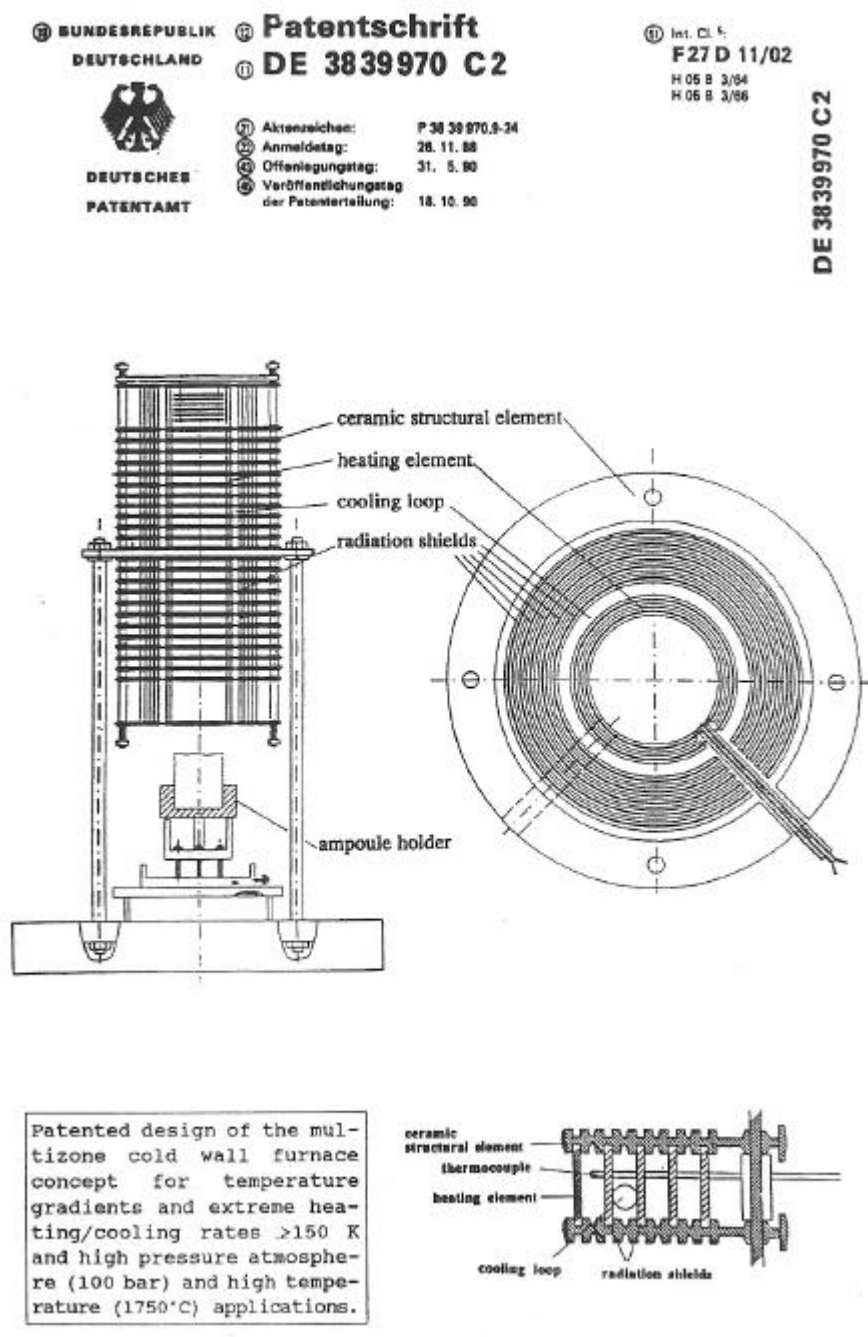


Figure 2: Patented design of the multizone cold wall furnace concept

After basic research, the MZCW Design was used in Crystal growing devices for GaAs and InP up to 4 inch in diameter.

The achievable high gradient of up to 150 K/cm in tough systems makes it an interesting technology for High Temperature Super Conductors (HTSC), too. A 3-zone furnace was used for texturing HTSC Material at the Research Center Karlsruhe.

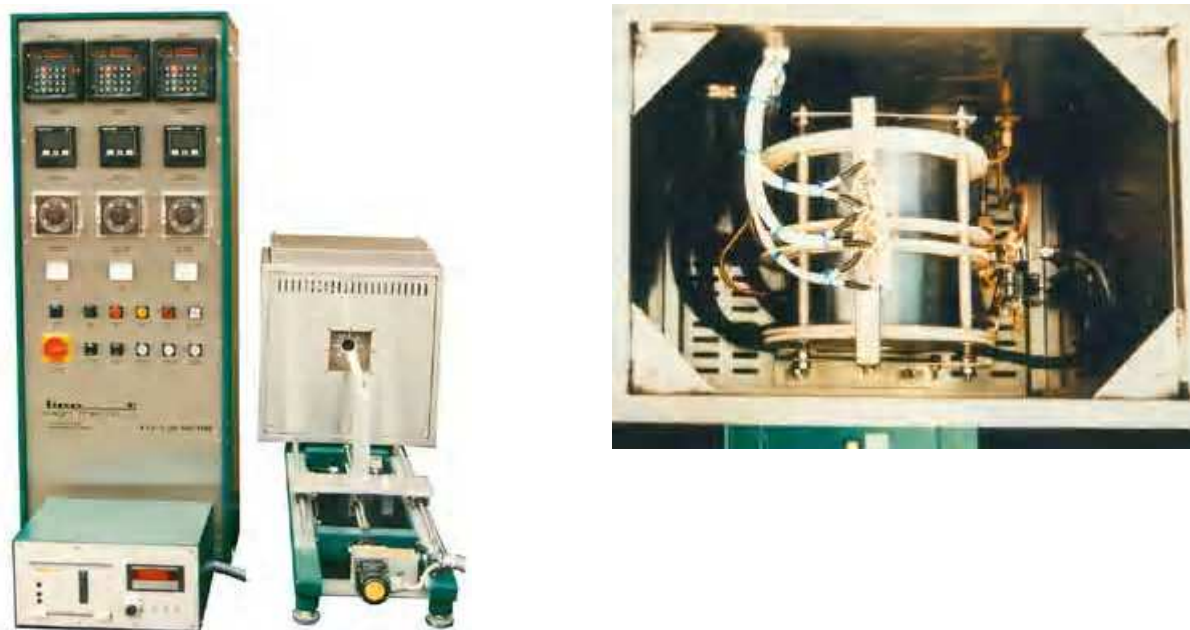


Figure 3: 3-zone high gradient furnace for texturing of HTSL

But the main result, based on tests and experiences with the MZCW crystal growing furnaces, was the possibility to simplify the concept and to adapt it to industrial application . The number of zones was reduced to nine and standard fibre insulated heating modules are used now.



Figure 4 :VGF-furnace, 18-32 zone, Tmax 1350 °C, 2 - 100 bar

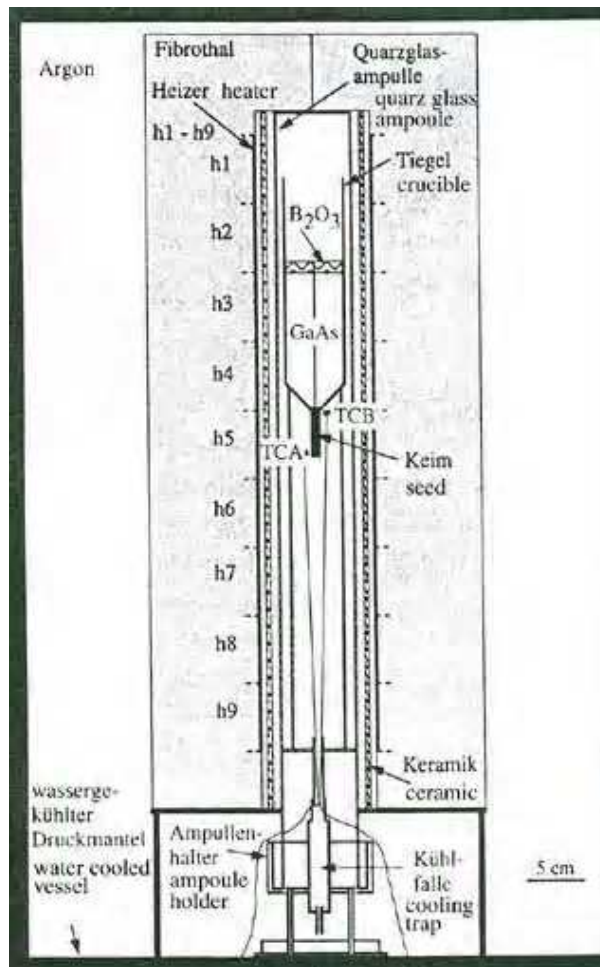


Figure 5: Design for industrial VGF-furnace

Today the VGF technology is already in the production stage in industry and is gaining considerable market shares.

2.2 Crystal growth of silicon carbide (SiC)

Silicon carbide, one of the newest semiconductors used in technology, is not easy to grow, and more than 250 modifications are known, but in comparison to traditional semiconductor material like silicon or GaAs it offers several advantages.

Because of its high thermal conductivity SiC is one of the most interesting materials for power electronics. Power densities up to 100 times of that of silicon are possible.

It's the material of choice for high temperature electronics. Silicon carbide devices are thousand times more insensitive against radiation and can be used up to 600 °C. This enables the integration of intelligent sensors in aerospace industry (turbine engines, long term space missions), automobile industry (motor) or in nuclear plants

SiC is the favourite substrate material for optoelectronic devices, especially for blue LED and UV photo diodes.

Growing crystals of silicon carbide by sublimation is a common technology, because the liquid phase requires very high temperatures and pressures. The standard way of crystal growth is the modified Lely process.

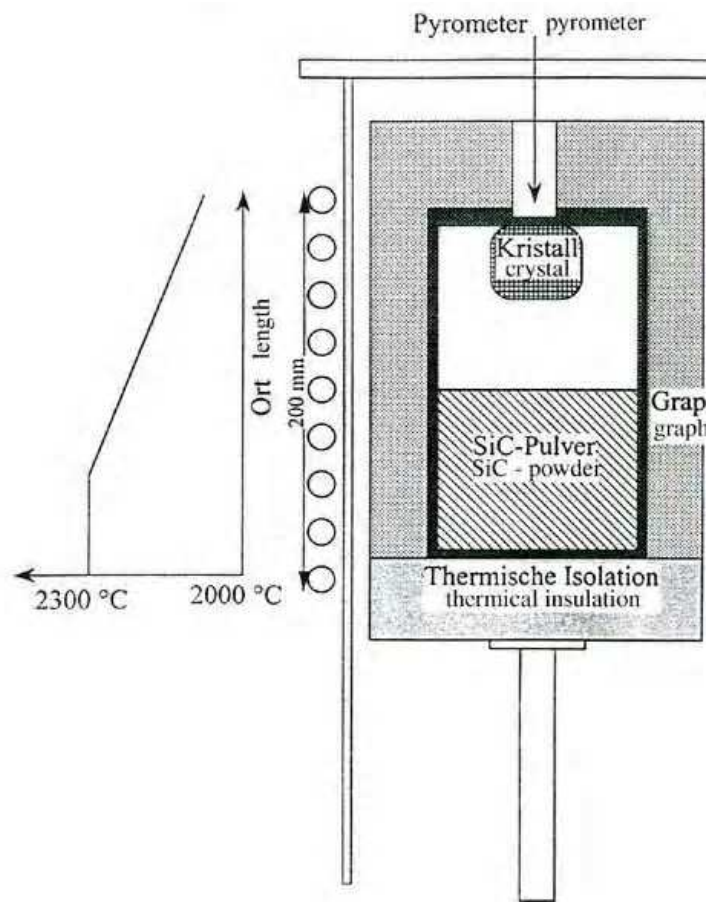


Figure 6: Principle of silicon carbide sublimation growth



Figure 7: Laboratory- crystal growth furnace for SiC

In this process the complete construction is build in a cylindrical glas tube with two walls.

Between the walls water is flowing in order to cool the cavity. The cavity (length 400 mm, diameter 300 mm) filled with a crucible (graphite), is heated by induction (heater length 200 mm). The temperature inside the crucible is higher than 2300 °C with a radial gradient of 10 to 50 K/cm. In comparison to the standard Lely procedure a SiC seed crystal is fixed at the top in order to fix the orientation of the crystal product and to reduce the density of defects. Inside the crucible SiC source powder is filled in. In order to avoid oxidation the chamber is evaluated down to 10^{-5} mbar at the beginning of the process and flooded with argon at the growth stage. Nitrogen can be added if doped SiC is required.

Varying parameters of this heating process are the frequency and the resulting skin effect. Besides that, the temperature gradient in z-direction can be changed as well. For more flexibility the crucible can be translated in vertical position and rotated.

The complete process is controlled directly by the front panel electronic device and a connected computer. There are expansion possibilities like measurement capturing and analysis.

Linn High Therm has built systems for growing SiC crystals of up to 3 inch and 4 inch in diameter. Growing speed is around 0.1 to 0.5 mm per hour (1 mm/h). Maximum length of the crystal is about 30 mm.



Figure 8: Production crystal growth system for 2" SiC-crystals (4H/6H)

The crystals obtained by gas phase growth are suitable for industrial use, but the gains are restricted by defects like micropores. To overcome this problem realized a new idea and the Chair of Electrical Engineering Materials, Linn High Therm, and Wilden Engineering made a project to develop a system to prepare SiC out of an oversaturated melt of silicon. The source of the carbon is the crucible itself.

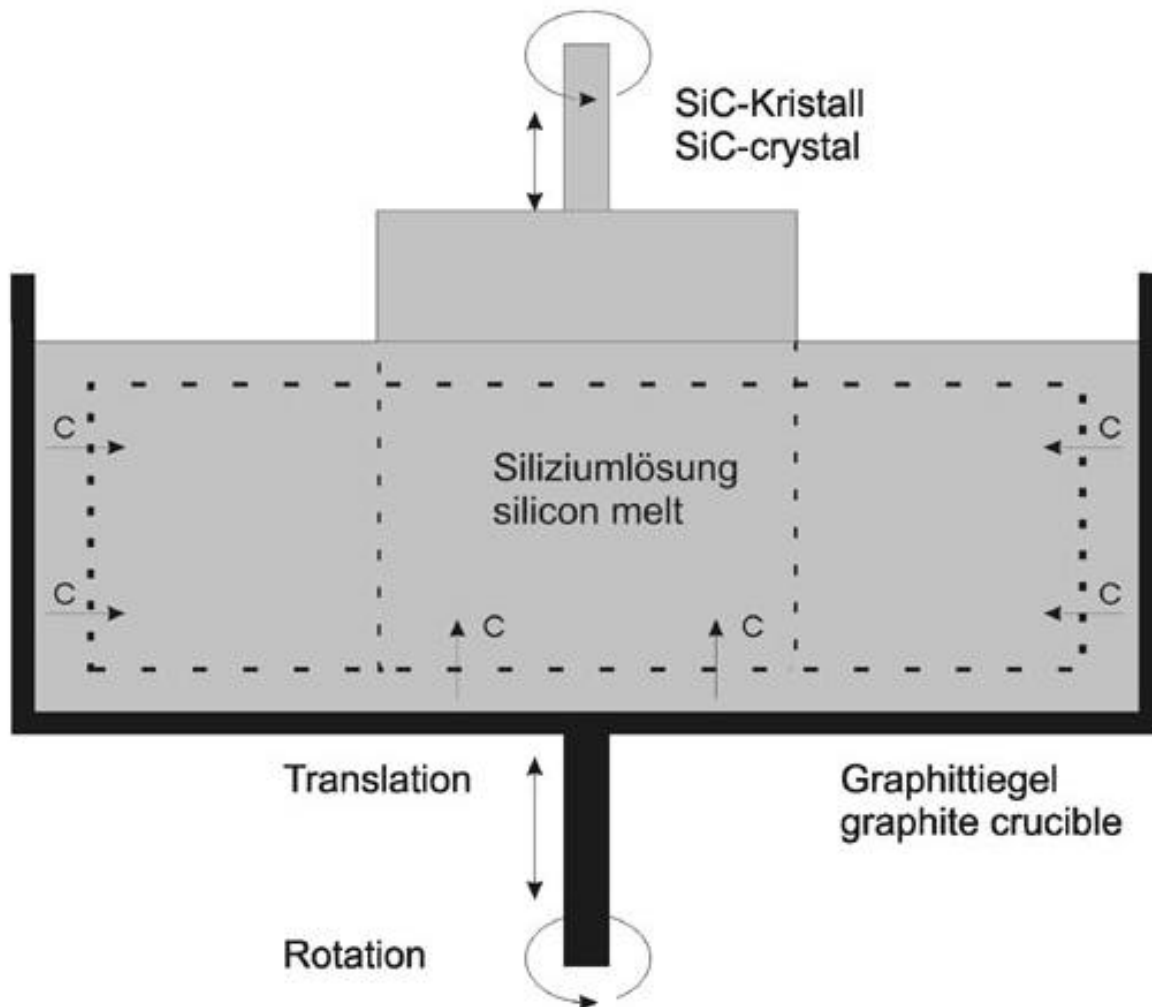


Figure 9: Principle of SiC-solution growth

Extensive calculations at Erlangen University concerning vapour pressure of silicon at high temperature, thermal field, geometry and behaviour of melt leads to a high temperature, high pressure system up to 2300 °C and 200 bar following the TSSG-methode (top seeded solution growth). The rotation frequency is 0 - 300 rpm and the translation speed is 1-100 mm/day. Despite the high requirements in temperature and pressure the fluctuation of rotation and translation must be very low.



Figure 10:

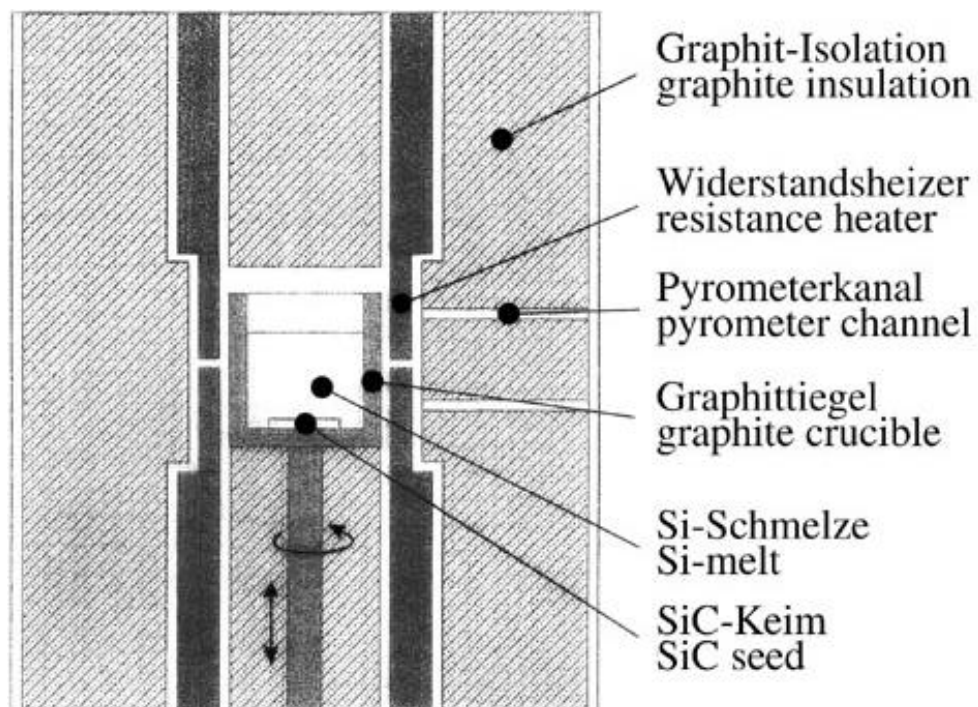


Figure 11:

First results are very promising. Micro pipes in the seed are getting closed during the growing process and dislocation density is significantly decreased compared to gas phase growth.

3 Micro-crystal growth system



Figure 12: IFGRV-120/220/2300

For the production of single crystalline fibers ($\varnothing = 0,2-2,0$ mm, $l_{\max} = 250$ mm) according to the micro pulling down process, 2000 mg of starting material (minimal quantity approx. 250 mg) is melted in a platinum crucible (for high-melting compounds also Ir-, W-, Mo- crucibles could be used) and a fiber crystal is pulled down through a capillary nozzle in the crucible bottom. Pulling rates are variable from 0,05 - 20 mm/h. The heating zone is installed inside a quartz chamber, allowing growth under vacuum or protective gas atmospheres and convenient visual control.

- very high crystal growth rate and process stability
- low energy and material consumption
- cylindrical and also "ribbon-like" crystal shapes are possible
- remarkably lower investments into crystal growth equipment compared to other crystal growth processes
- excellent for crystal growing research.

control device: temperature program controller

power unit: primary heater 80 W (max. 500 W), secondary heater 30 W (max. 200 W)