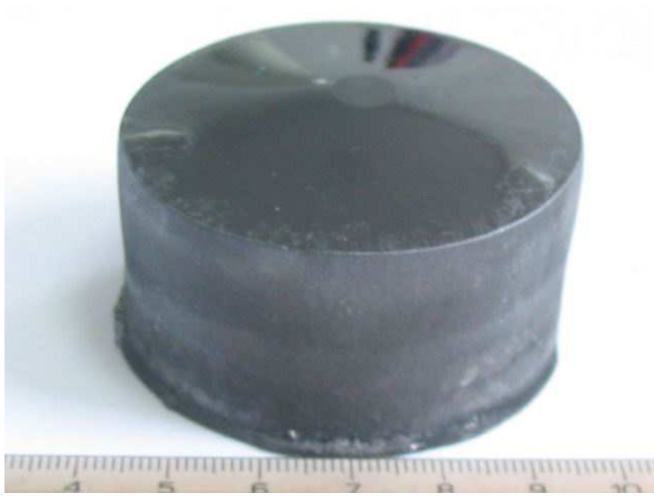
Software for Modeling of Long-Term Growth of Wide-Bandgap Crystals and Epilayers from Vapor

Virtual Reactor™



2011
STR-Group, Ltd.

Prehistory of STR:

1984: Start of the MOCVD modeling activities at Ioffe Institute, St. Petersburg, Russia

1993-1996: Group for modeling of crystal growth and epitaxy at University of Erlangen-Nuernberg, Germany

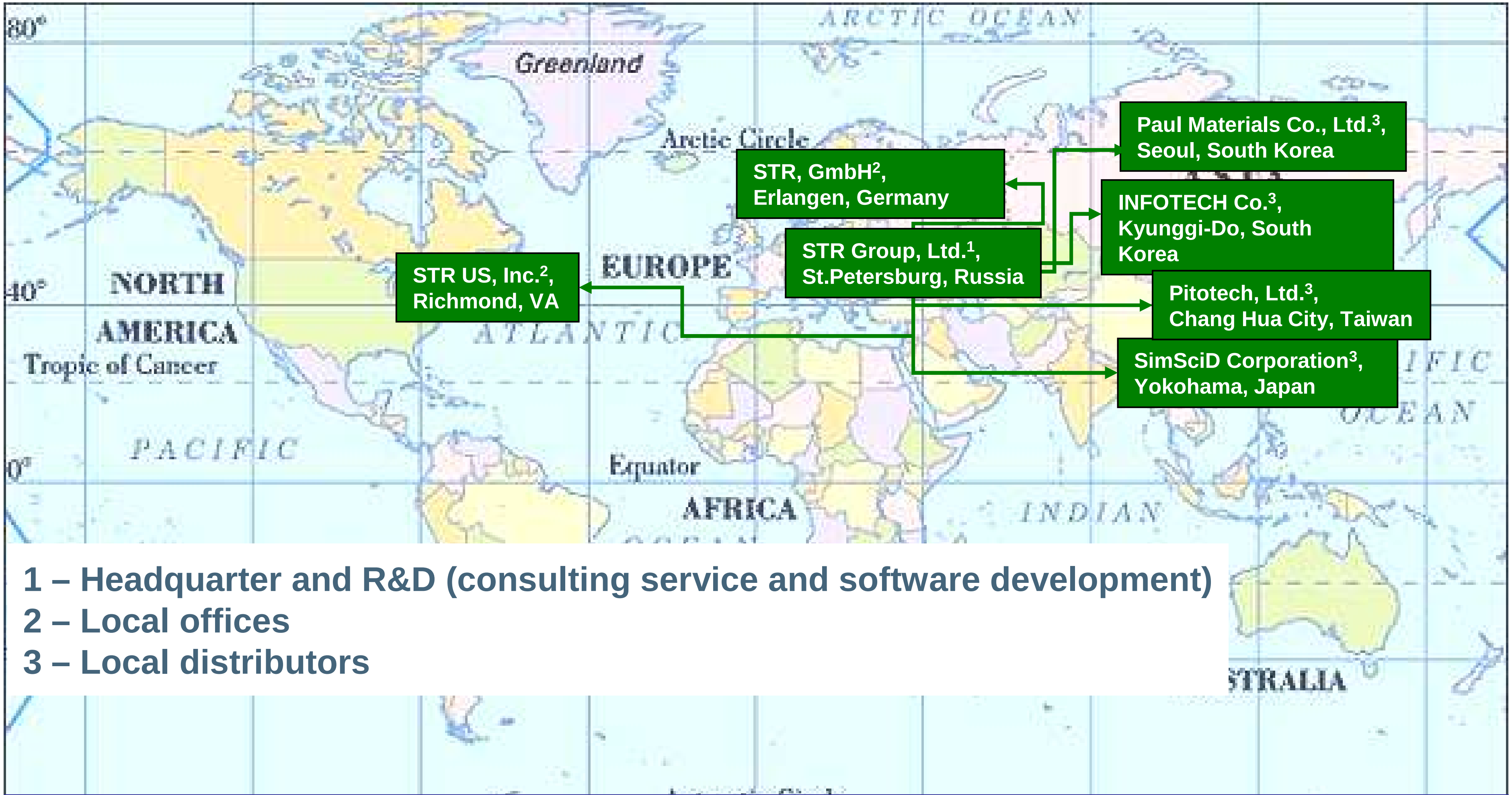
History of software development

2000: Launch of development of the first specialized software
2003: First release of commercial software package
2004: First release of the software for device engineering

STR Today:

More than 40 scientists and software engineers

STR Today



Bulk crystal growth modeling (Si, Ge, SiGe, GaAs, InP, SiC, AlN, Al_2O_3, Optical Crystals)

Epitaxy and deposition modeling (Si, SiGe, SiC, AlGaAs, AlGaInP, AlGaInN, high-k oxides)

Modeling of device operation (LEDs, Laser Diodes, FETs/HEMTs Shottky diodes)

Software & consulting services :

- Modeling of crystal growth from the melts and solutions: CGSim
- Modeling of polysilicon deposition by Siemens process: PolySim
- Modeling of bulk crystal growth of SiC, AlN, GaN: ViR
- Modeling of epitaxy of compound semiconductors: CVDSim
- Modeling of optoelectronic and electronic devices: SimuLED

Customer base:

- More than 100 companies and universities worldwide
- Top LED, LD and solar cell manufacturers
- Top sapphire, GaAs, GaP, GaN, AlN and SiC wafer manufacturers
- Top MOCVD reactor manufacturers

STR Virtual Reactor (VR) is a family of stand-alone 2D software tools designed for the simulation of long-term growth of bulk crystals and epilayers from vapor

Virtual Reactor editions:

- Physical Vapor Transport
  - For growth of SiC: VR-PVT SiC™
  - For growth of AlN: VR-PVT AlN™
- Hydride Vapor Phase Epitaxy: HEpiGaNS™
  - For growth of GaN
  - For growth of AlN and AlGaN
- Chemical Vapor Deposition
  - For growth of SiC: VR-CVD SiC™

Pennsylvania University (USA)
University California Santa Barbara (USA)
State Electrical-Technical University, Prof.Tairov (Russia)
Erlangen University (Germany)
Ioffe Physical-Technical Institute, Prof.Vodakov (Russia)
State Polytechnic University (Russia)
State University of New York at Stony Brook (USA)
Leibniz Institute for Crystal Growth, IKZ (Germany)
University of South Carolina (USA)
Linkoeping University (Sweden)
Meijo University (Japan)
Harbin Institute of Technology (China)
Dong-Eui University (Korea)
Ferdinand-Braun-Institute, (Germany)
Shandong University (China)
Warsaw University of Technology (Poland)
Yeungnam University (Korea)
……………………………………

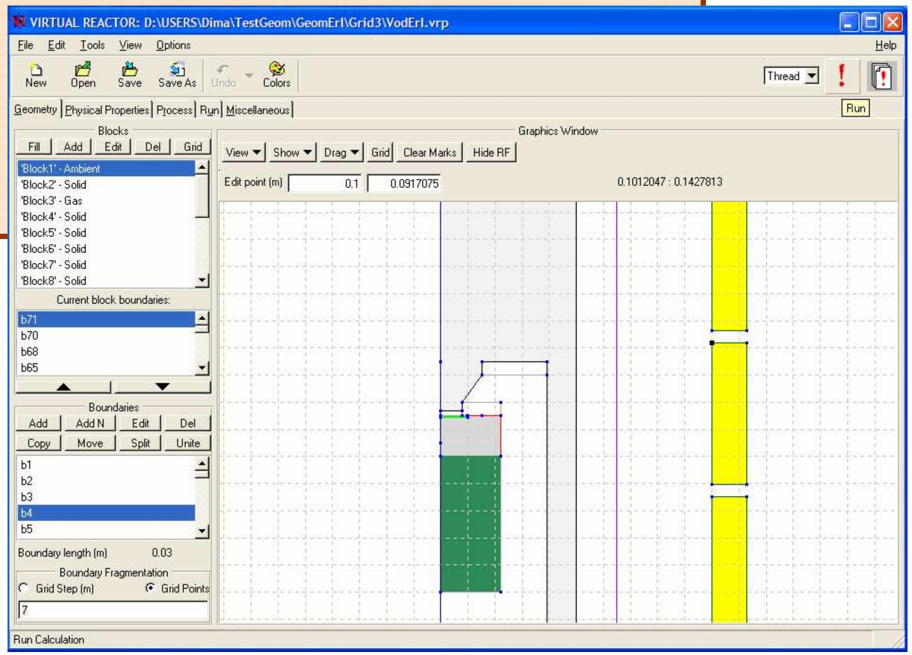
Materials Science Forum Vols. 483-485 (2005) pp. 47-52
online at http://www.scientific.net

SiC Crystal Growth by Sublimation Method with Modification of Crucible and Insulation Felt Design

Jung-Gyu Kim[a], Kap-Ryeol Ku[b], Dong-Jin Kim[c], Sang-Phil Kim[d], Won-Jae Lee[e], Byoung-Chul Shin[f], Geun-Hyoung Lee[g], and Il-Soo Kim[h]

Electronic Ceramics Center (ECC), Dept. of Information Materials Engineering, Dong-Eui University, San24, Gaya-dong, Busanjin-gu, Busan, 614-714, Korea

[a]205bug@hanmail.net, [b]20046247@deu.ac.kr, [c]dojakim@hotmail.com, [d]mrkim501@hotmail.com, [e]leewj@deu.ac.kr, [f]shinbc@deu.ac.kr, [g]iskim@deu.ac.kr, [h]ghl@deu.ac.kr



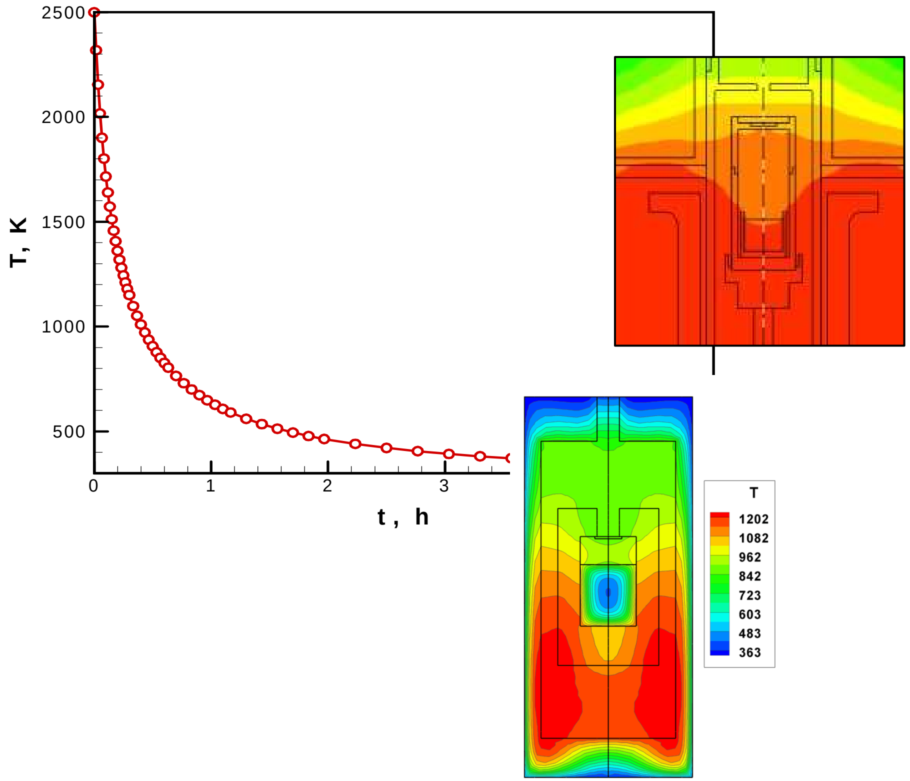
Industrial leaders in production of SiC, AlN, and GaN wafers

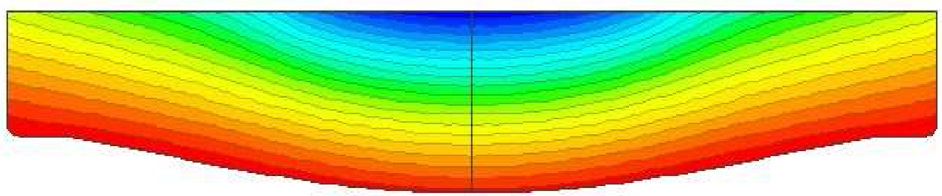
USA and Europe

CREE, Inc.
II-VI, Inc.
Dow Corning, Corp.
SiCrystal AG
The FOX Group, Inc.
Norstel AB
Crystal IS, Inc.
Nitride Crystals, Inc.
Semiconductor Crystals, Inc.
Freiberger Compound Materials, GmbH

Asia

DENSO, Ltd.
Nippon Steel Corp.
Bridgestone Corp.
Beijing Huajinchuangwei Electronics
Mitsubishi Electric Corp.
Showa Denko KK
Mitsubushi Chemical Corp.





VR is used now in many industrial companies in USA, Europe, and Japan

What are the problems solved by growth engineers? Where numerical simulation can be useful for practice?

Problem solved by growth engineers

Controllable inexpensive growth of high quality bulk crystals

- large (in diameter)
- thick (length)
- a necessary shape
- high quality

Major Physical Phenomena to be studied

- Heat transfer by conduction, convection and radiation
- Mixture flow and species diffusion through the gas region
- Non-steady state effects typical for bulk crystal growth
- Growth rate prediction control. Problem of polycrystal deposition. Crystal shape evolution in long-term growth. Porous source operation
- Formation and Evolution of defects in long-term growth

Models commonly used in simulation of crystal growth

- Modeling of heat transfer in the overall growth system
- Modeling of mixture flow in the reactor
- Modeling of species mass transport by convection/diffusion
- Models of homogeneous chemical reactions
- Thermal elastic problem

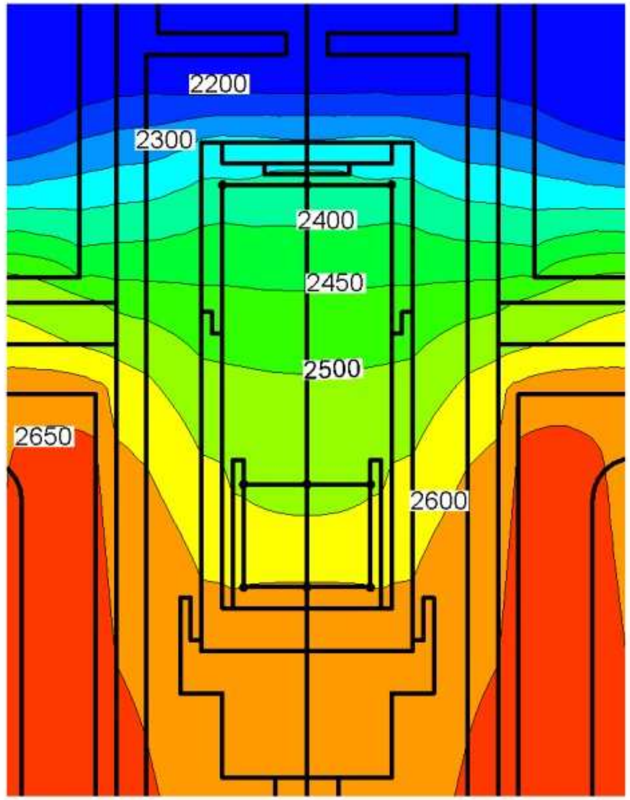
Advanced models developed by STR

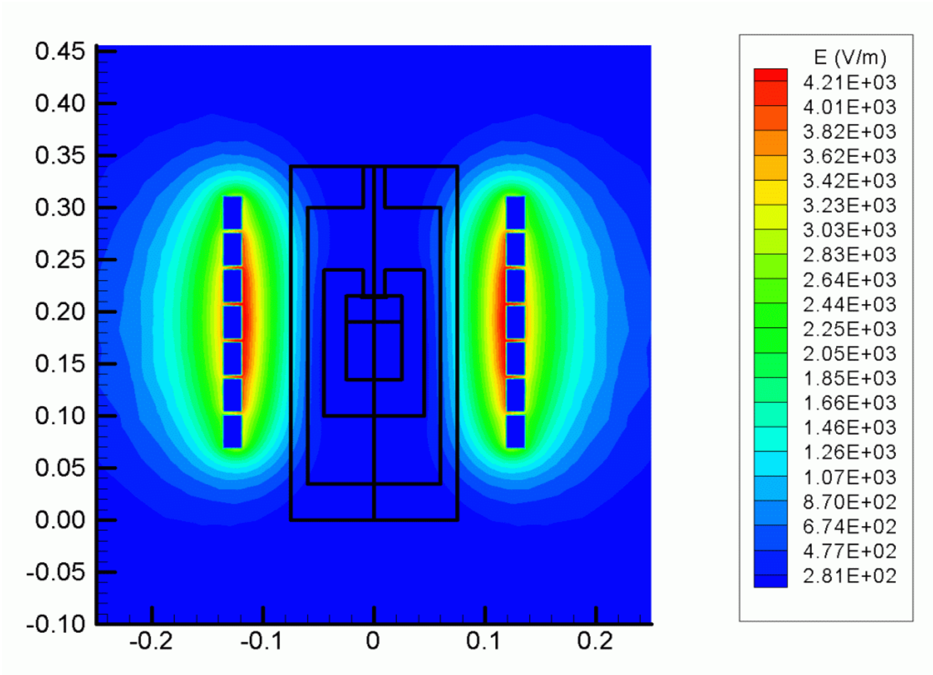
- Account of non-steady character of long-term growth process
- Prediction of the crystal evolution
- Advanced models of heterogeneous chemistry
- Prediction of the parasitic phase deposition
- Modeling of species mass transport in porous reactive medium
- Analysis of dislocation evolution

VR is the Unique Software Package

Heat- and Mass Transport Modeling

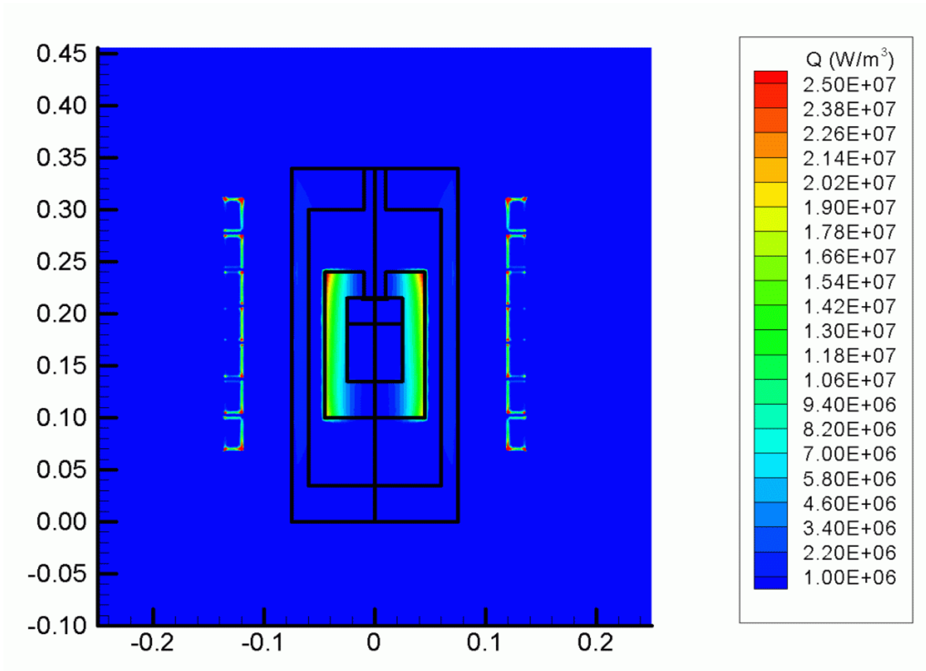
- **Heat transfer mechanisms**
  - Heat conduction in isotropic and anisotropic media
  - Radiation
  - Convection
- **RF heating** with non-uniform heat distribution in the crucible by a single coil or several independent coils
- **Temperature fitting** at one or several reference points
- **Unsteady Module** for simulation of heating of the growth system before the crystal growth and cooling after the crystal growth





Electric Field Distribution

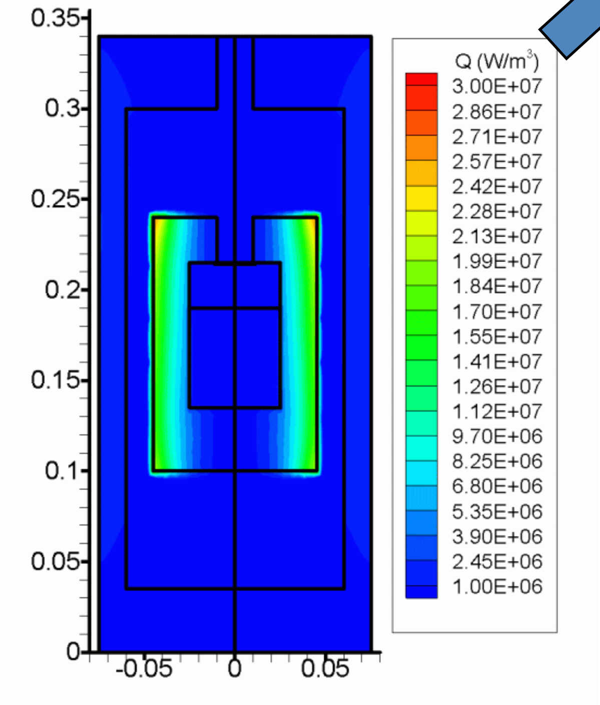
Joule Heat Source Distribution



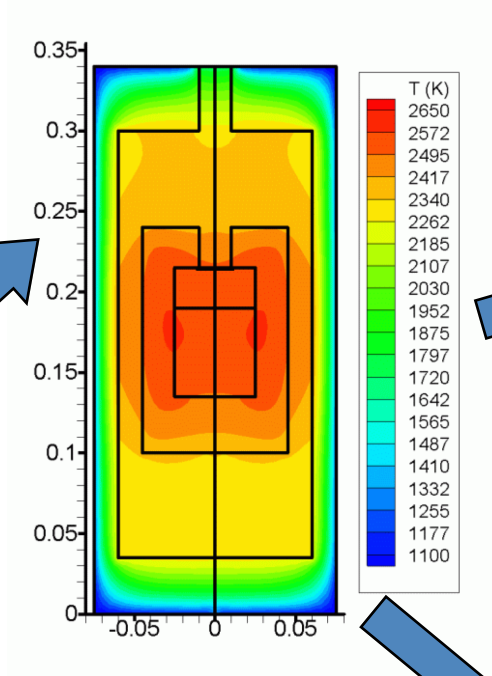
Coil in the basic position

Temperature in the seed center is maintained at 2500 K

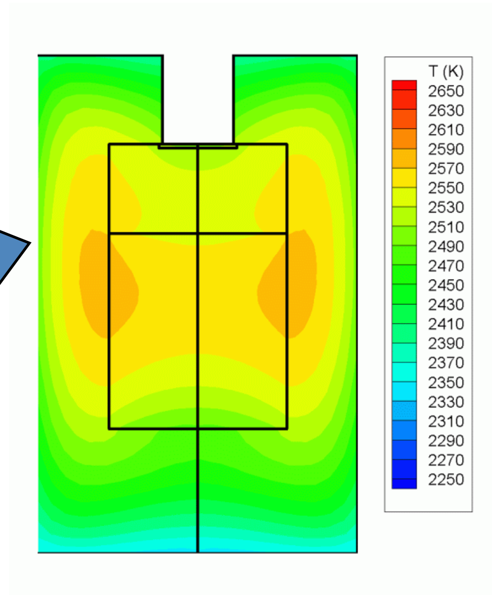
Joule Heat Source Distribution



Overall growth system

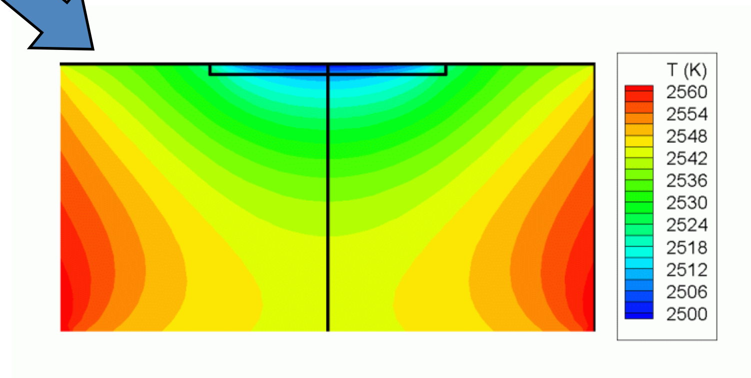


Crucible



Temperature distribution

Growth chamber

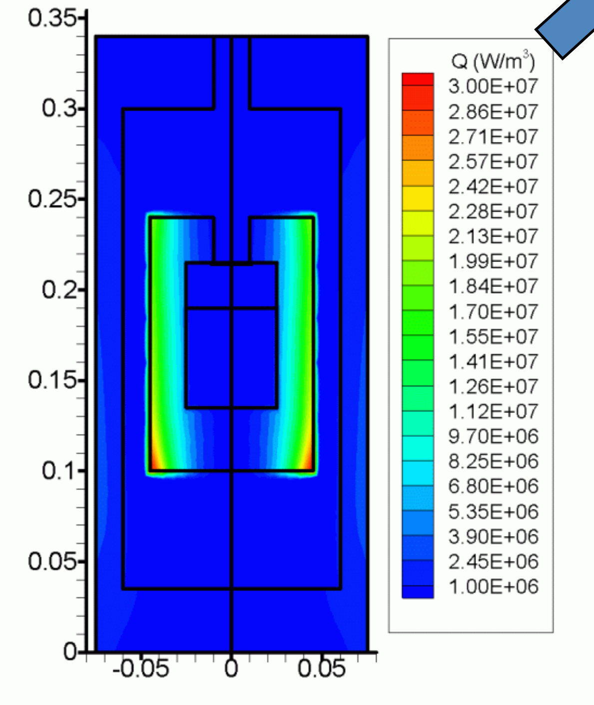


RF Heating Modeling: Effect of the Coil Position

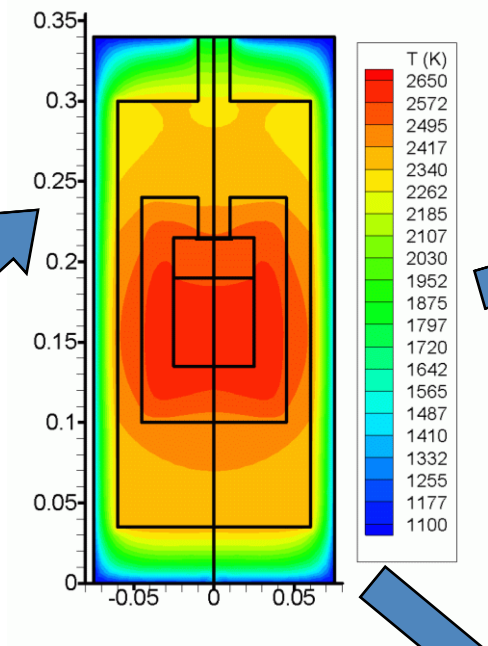
Coil lowered by 50 mm

Temperature in the seed center is maintained at 2500 K

Joule Heat Source Distribution

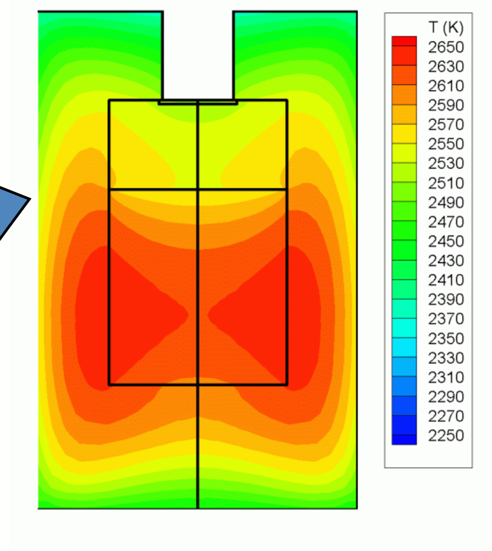


Overall growth system

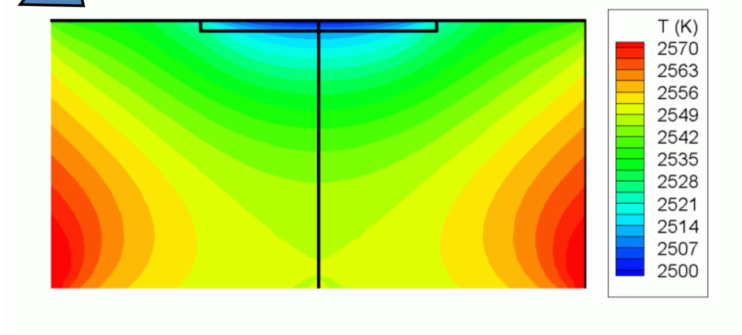


Temperature distribution

Crucible



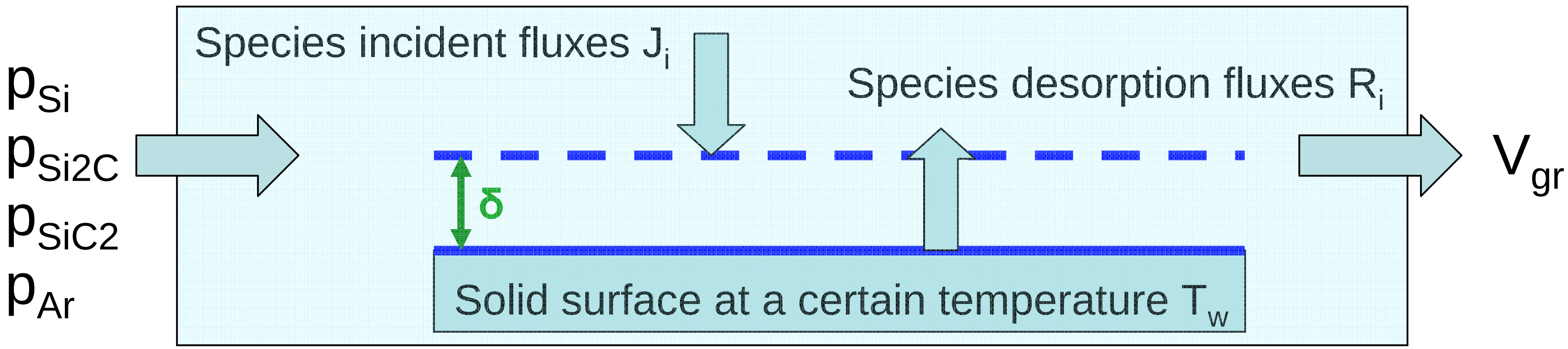
Growth chamber



Simulation of species mass transport and heterogeneous chemical processes

Where accurate modeling of heterogeneous chemistry is necessary?

- **Crystal growth**
- **Polycrystal formation on crucible side walls**
- **Graphite etching. Etching can provide additional supply of carbon atoms to the crystal**
- **Sublimation and graphitization of powder granules. Recrystallization of vapors on granule surface**



Advanced model of heterogeneous chemical processes

Basic assumptions

- The atoms in the adsorption layer are nearly in thermodynamic equilibrium with the crystal: atom incorporation and desorption rates are much higher than their difference, i.e. the crystal growth rate
- Use of quasi-equilibrium heterogeneous reactions
- Growth occurs under mass-transport limited conditions

Advantages

- Unified approach is used for wide spectrum of growth technologies (PVT, HVPE, CVD, and MBE) and materials grown from vapor phase at high temperature
- Simulation does not require detailed info on chemistry kinetics. Material database supplied together with the s/w contains accurate data on species characteristics

- **Species molar fluxes:**

$$F_i = \alpha_i \beta_i \left(p_i - p_i^0 \right)$$

α_i - i-th species sticking coefficient

β_i - the Hertz-Knudsen factor

p_i - i-th species partial pressure

p_i^0 - i-th species equilibrium pressure

- **Mass action law for the equilibrium pressures**

$$\prod_{i=1}^{N_s} \left(p_i^0 \right)^{\gamma_{ir}} = K_r(T)$$

$K_r(T)$ - equilibrium constants

- **Stoichiometric atom incorporation**

$$\sum_{i=1}^{N_s} f_{ie} F_i = \rho_c \frac{N_A}{M_c} V_g x_e$$

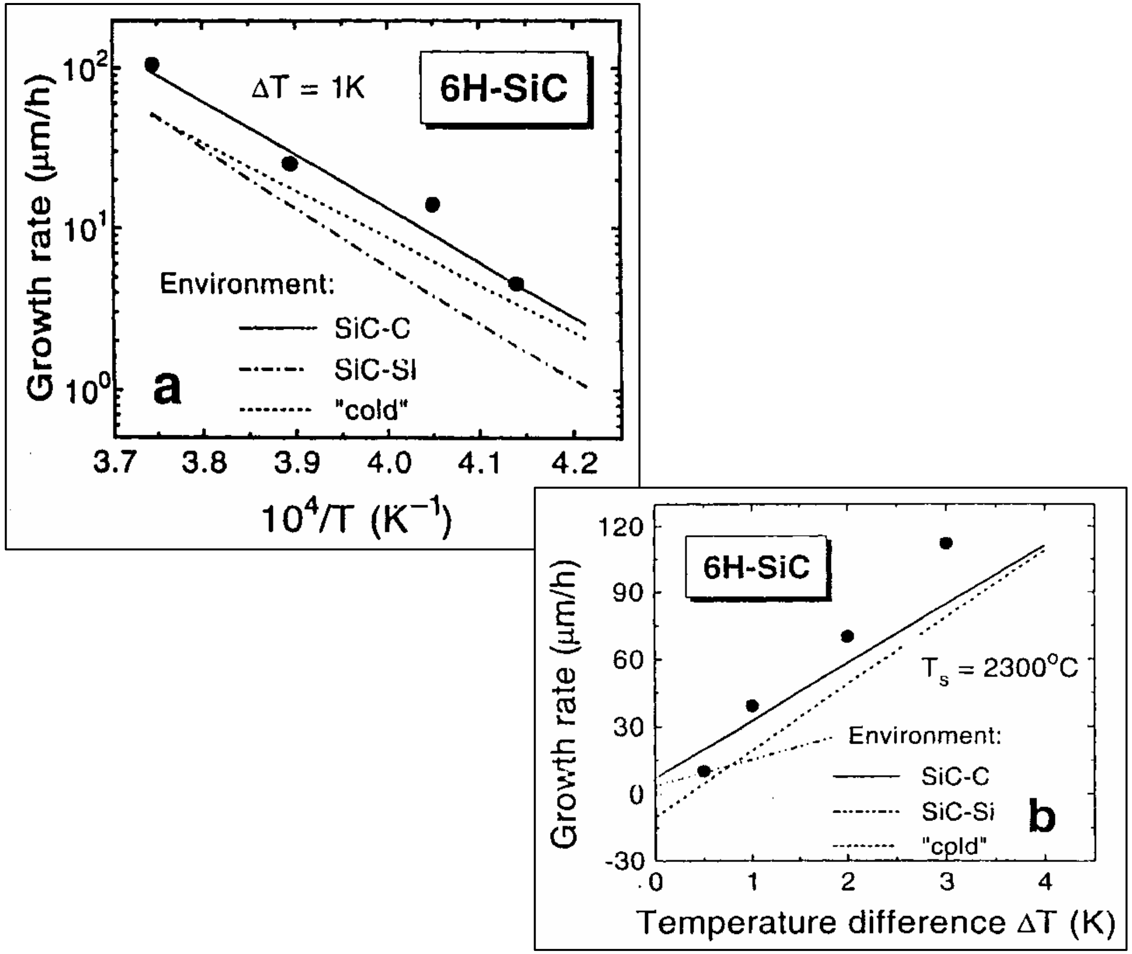
f_{ie} - number of atoms of e-th element in a molecule of i-th species

ρ_{cr} - crystal density

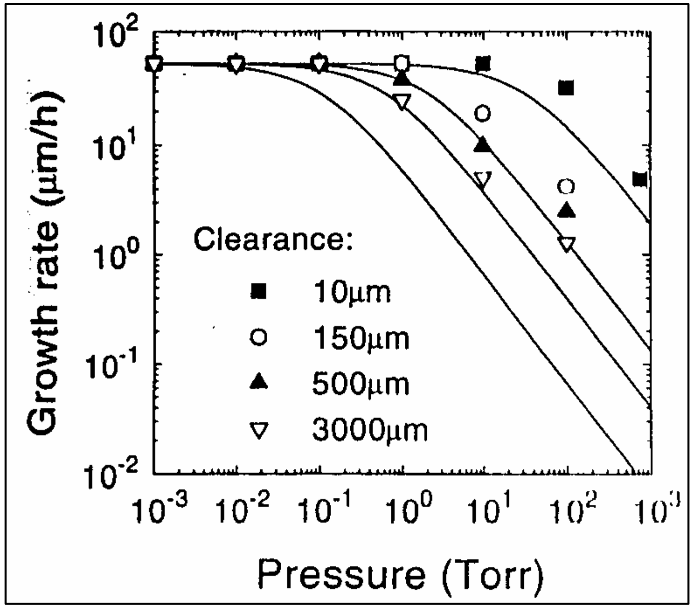
M_{cr} - crystal molar mass

V_{gr} - growth rate

Models of Mass Transport were verified using experimental data of SiC growth by Sublimation Sandwich Method



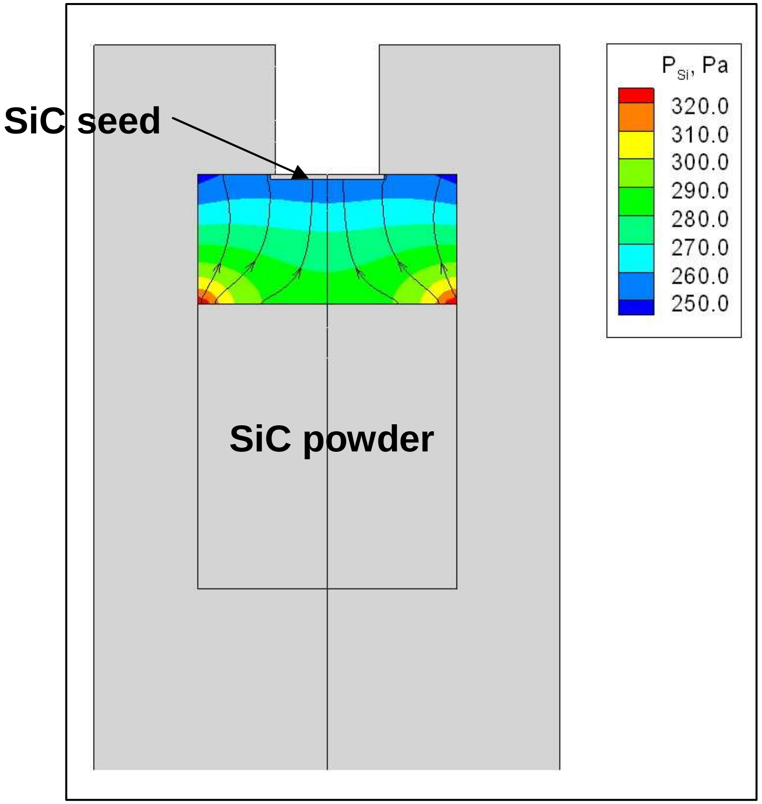
Growth rate vs. growth temperature (a) and temperature drop between the source and substrate (b). Lines and circles present theoretical predictions and experimental data, respectively.



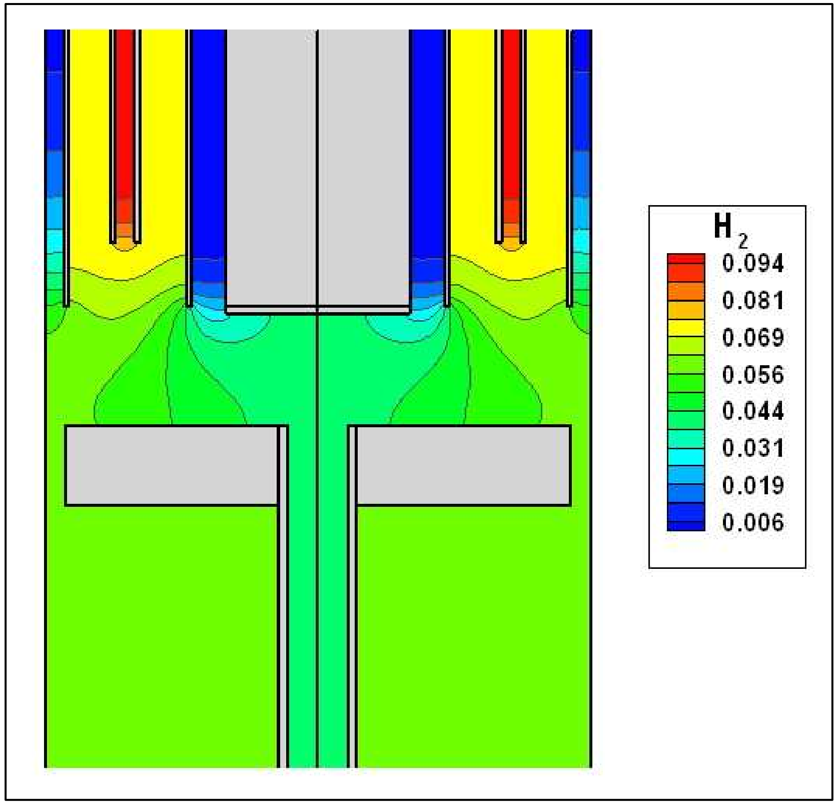
Growth rate vs. the total pressure

A. Segal et al., J. Cryst. Growth (2000)

Examples of Species Mass Fraction Distributions



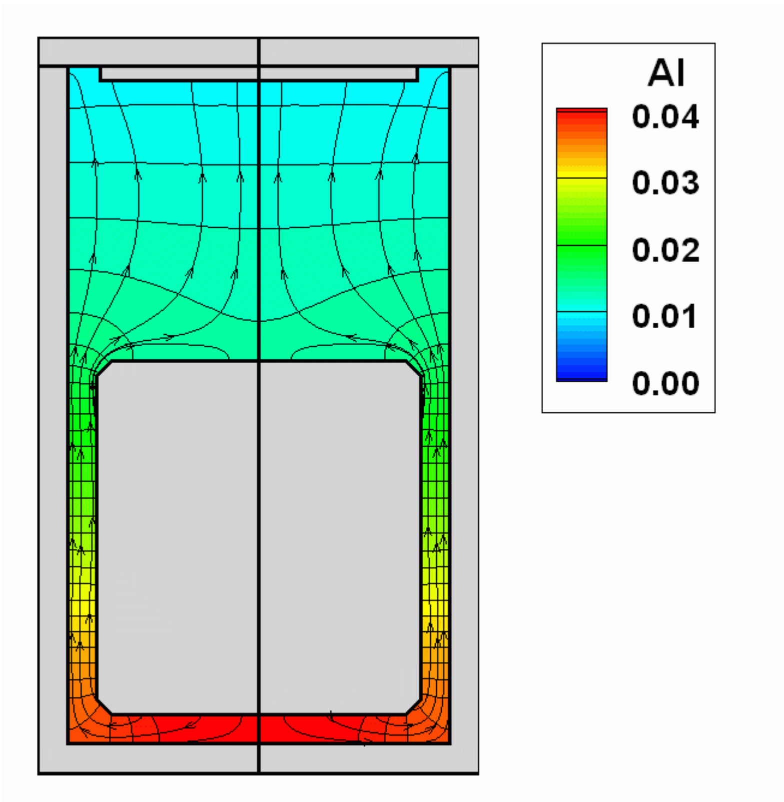
Si distribution in PVT SiC

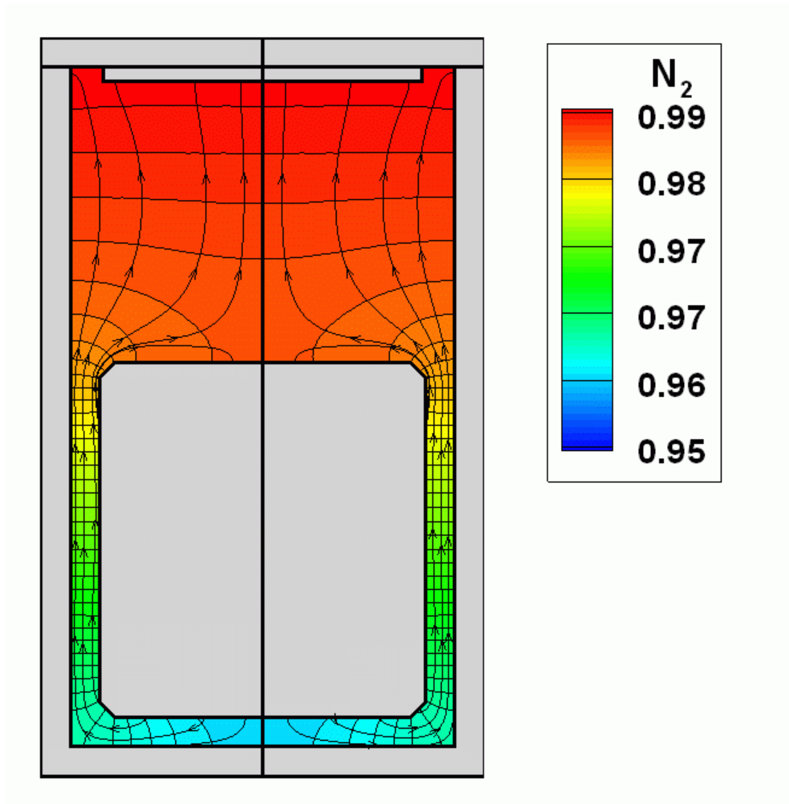


H_2 distribution in HVPE GaN

Flow Pattern and Species Distribution in the Growth Chamber

High pressure: P = 600 mbar





Non-steady state Effects in Bulk Crystal Growth

Transient Effects in Bulk Crystal Growth

Internal Effects:

- Enlargement of the crystal
- Deposit formation
- Source consumption (in PVT growth)

External Effects:

- Movement of the inductor coils or some parts of the reactor
- Variation of the operating conditions during the growth (T, p)

Applicability of the Quasi-Steady-State Approach:

Characteristic time of establishing of steady-state distribution inside the crystal growth system is much less than the characteristic time of variation of geometry, coil position and process parameters

Basic Concept

- Continuous growth is presented as a series of consecutive time steps
- Specification of the operating parameters (coil position, reference temperature, total pressure, etc.) for each time instant
- Modeling of steady-state heat- and mass-transfer at each time step
- Moving of all solid surfaces (crystal, source, deposits) due to growth/sublimation using the results of computations
- Change of the reactor geometry or/and operating conditions according to the user specifications
- Regeneration of the computational grid in all zones with changed geometry

1st stage

Definition of the geometry and properties

Material database

2nd stage

Definition of the parameter variation

For each time step

3rd stage

- Computational grid generation
- Coupled computation
  - Heat transfer with inductive heating
  - Convection and species transport in the growth chamber
- Prediction of deposit formation
- Crystal shape modification
- Update of growth conditions and location of furnace units and heaters

4th stage

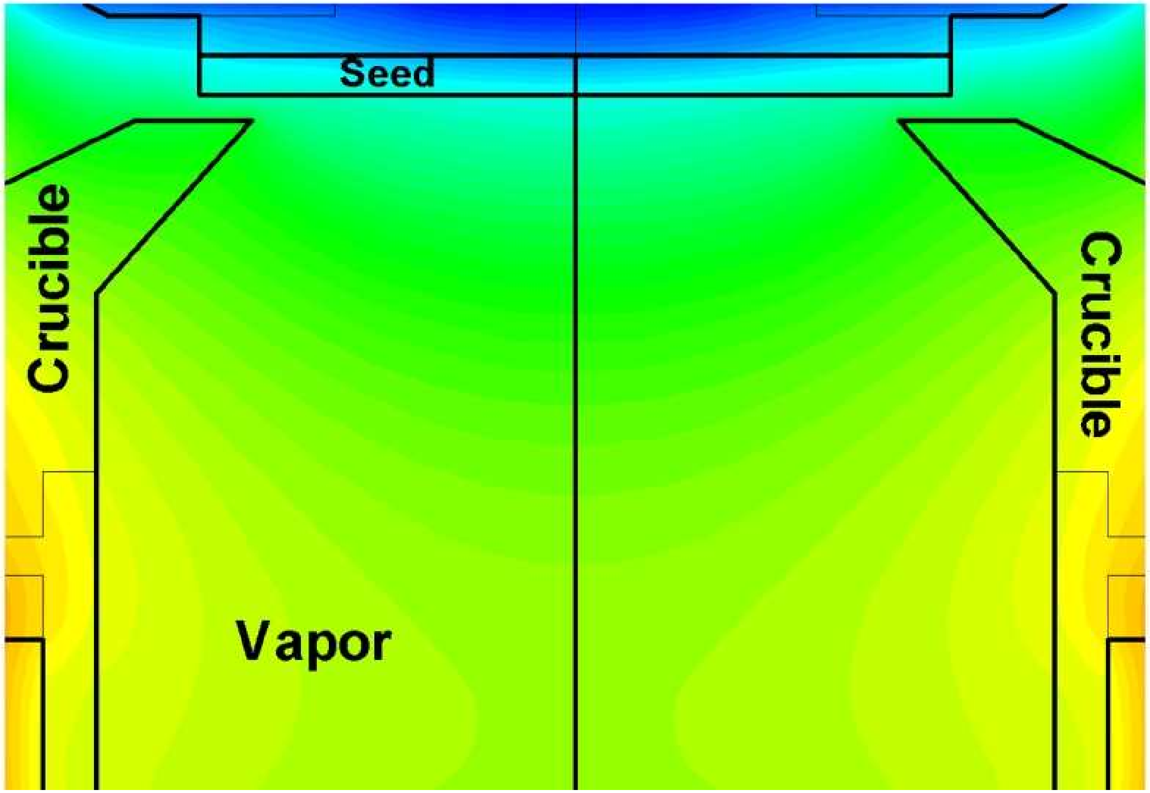
Analysis of
- Thermal elastic stress
- Gliding and threading dislocations

Simulation of Crystal Shape Evolution

Crystal Enlargement in a SiC Growth System

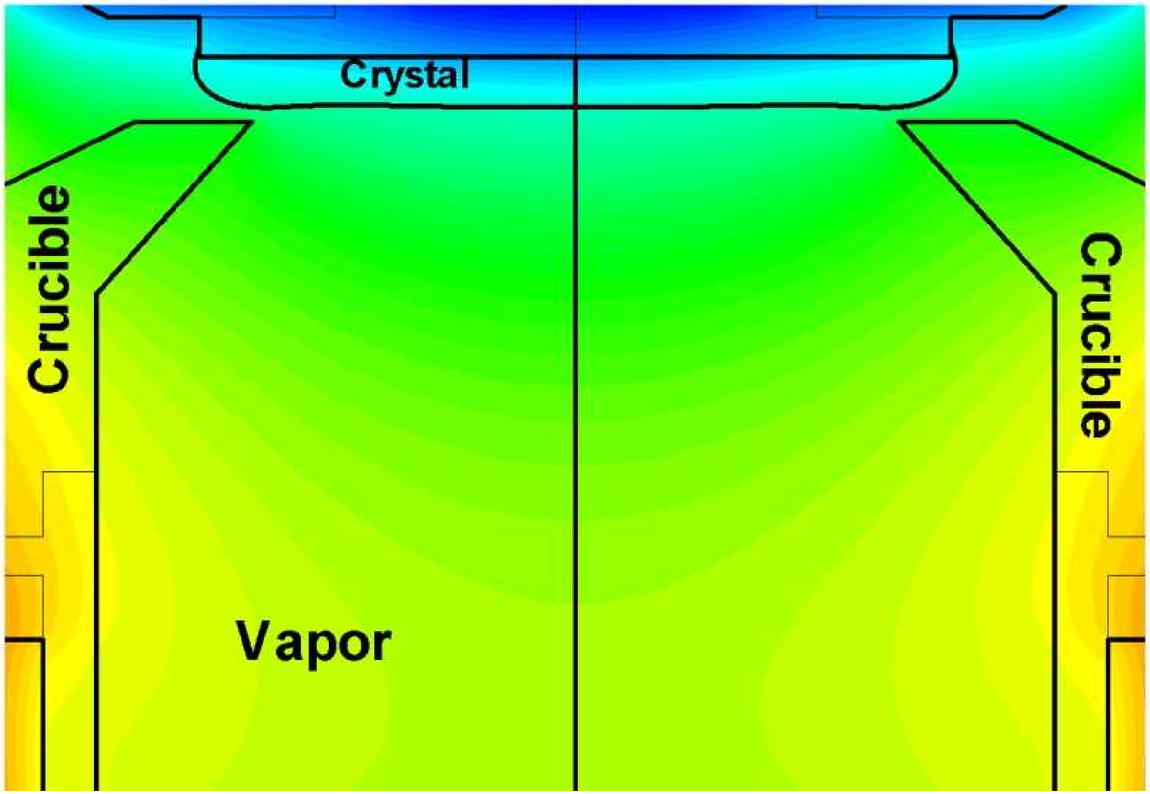
Start of the growth

t = 0



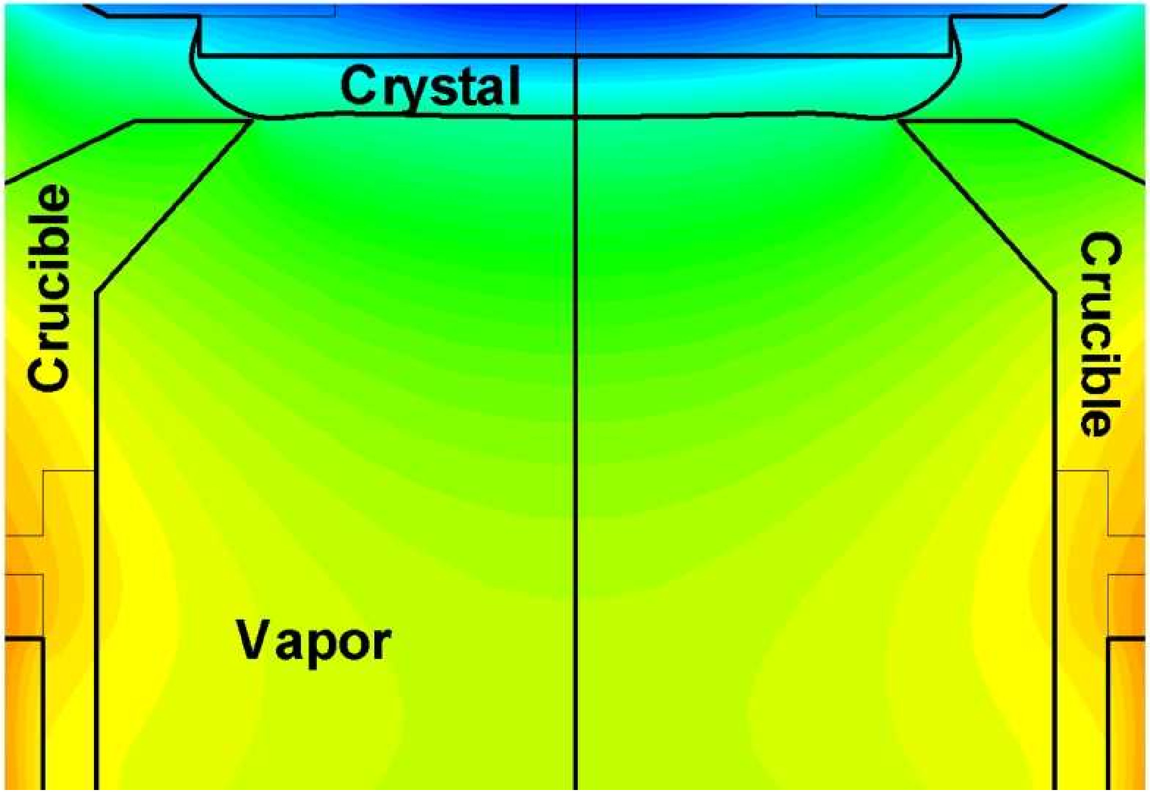
Crystal Enlargement in a SiC Growth System

t = 2 h



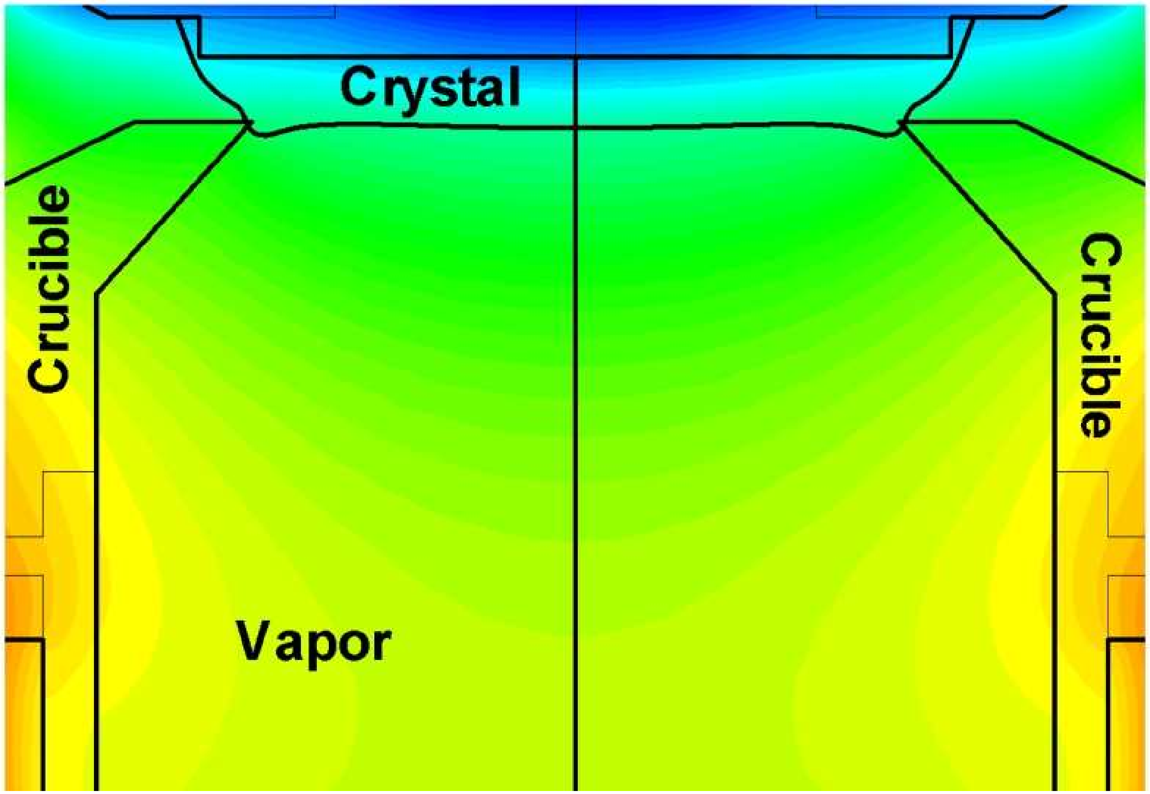
Crystal Enlargement in a SiC Growth System

t = 4 h



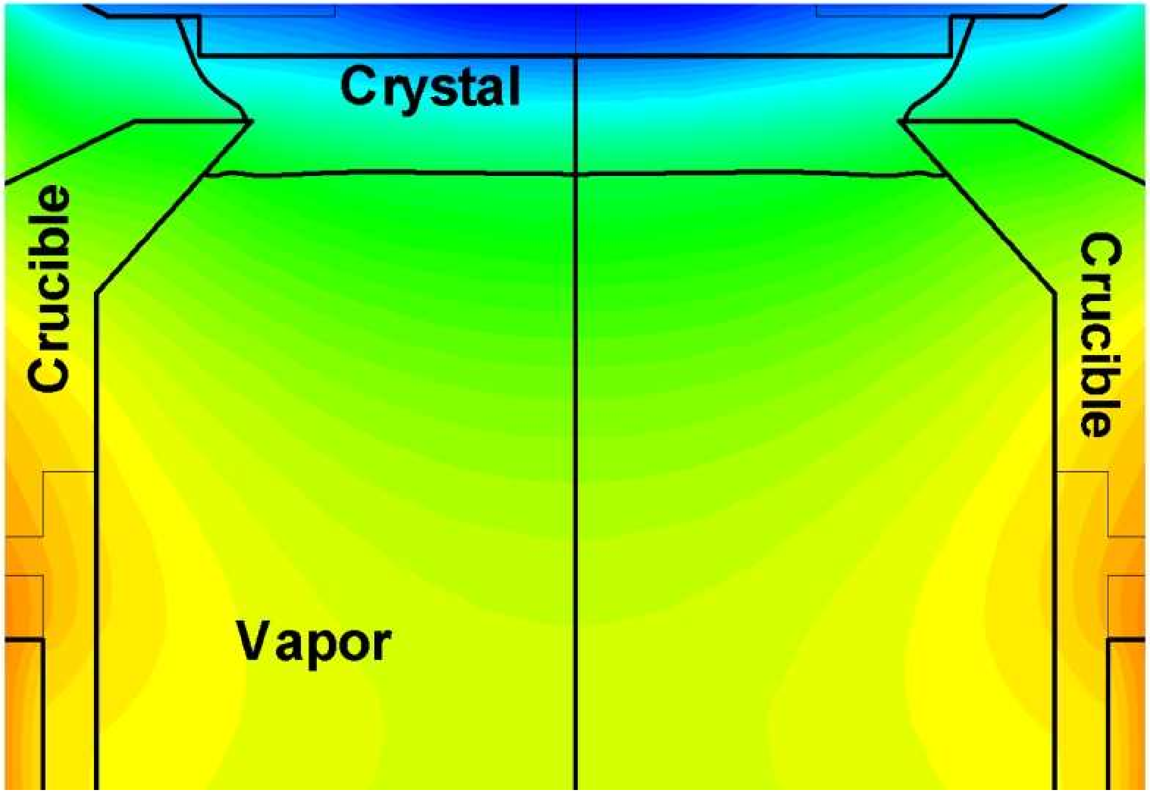
Crystal Enlargement in a SiC Growth System

t = 6 h



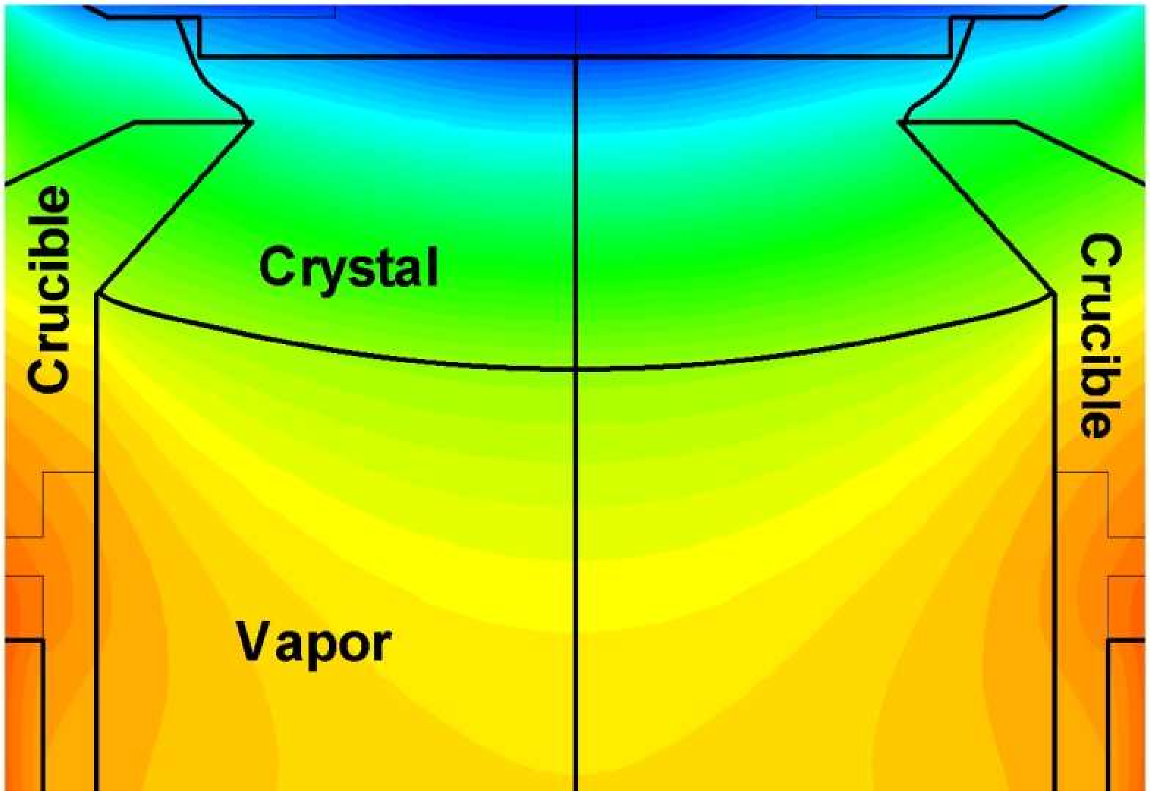
Crystal Enlargement in a SiC Growth System

t = 10 h



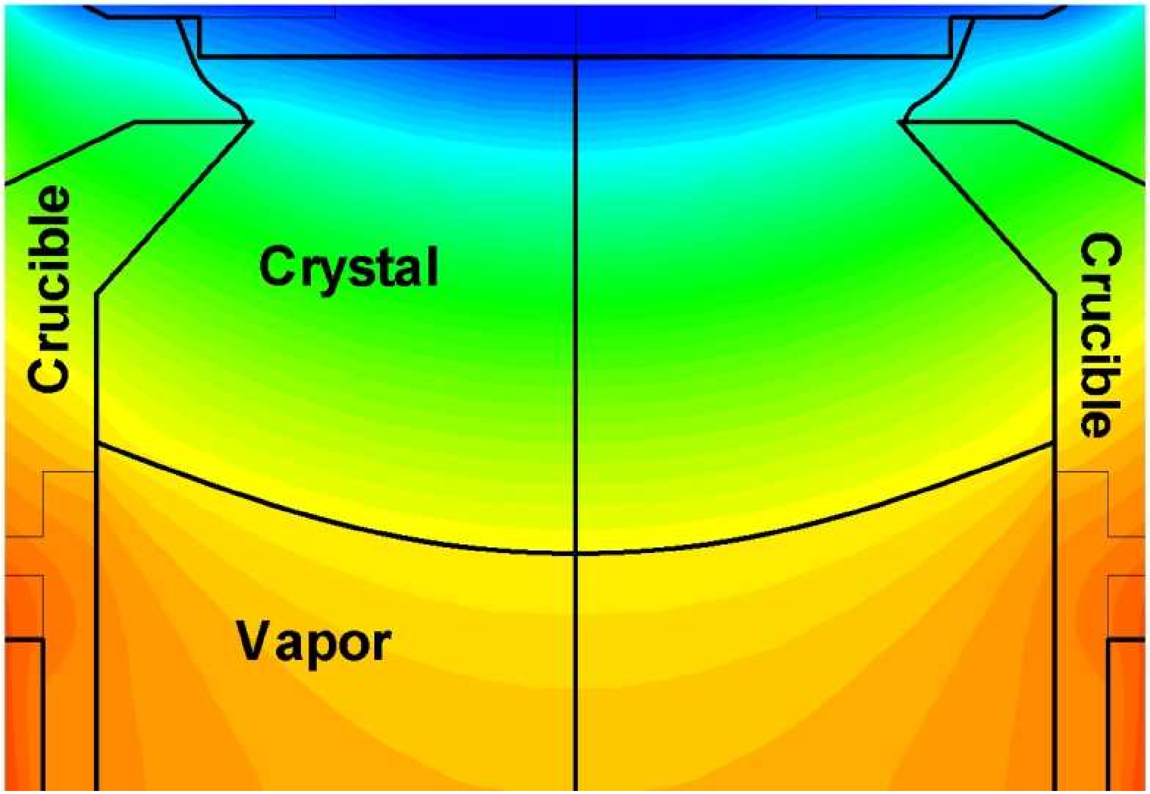
Crystal Enlargement in a SiC Growth System

t = 20 h



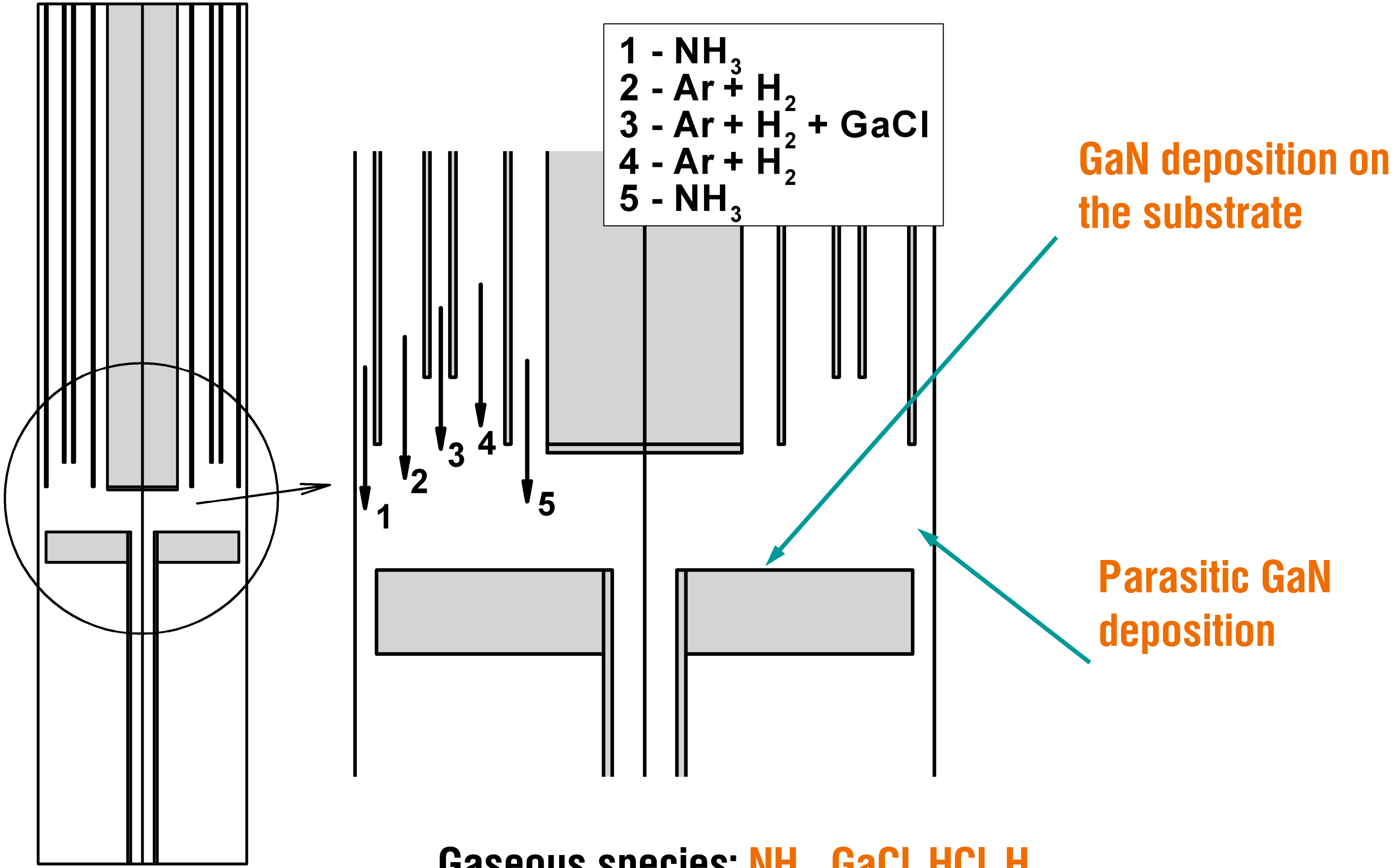
Crystal Enlargement in a SiC Growth System

t = 50 h

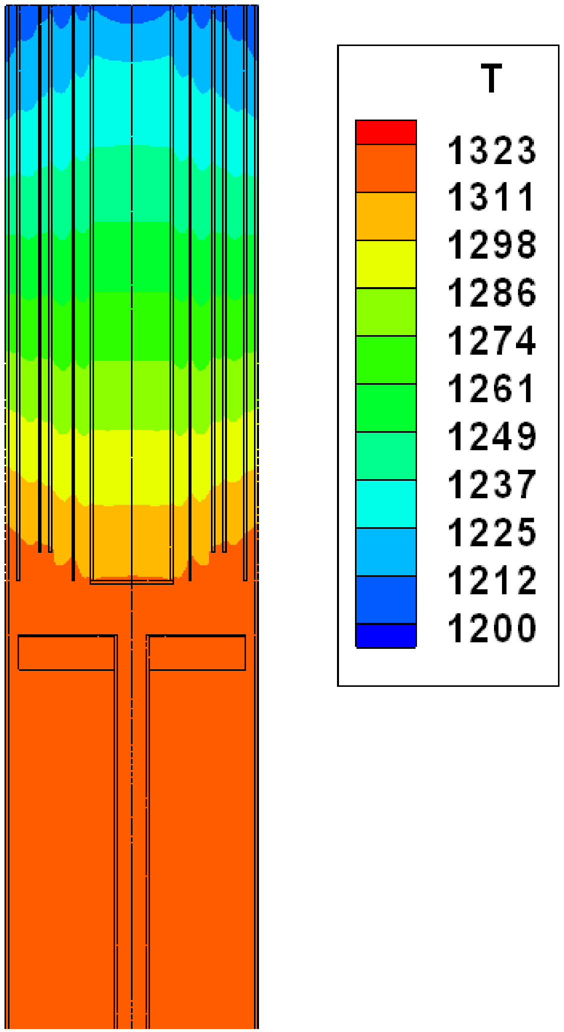


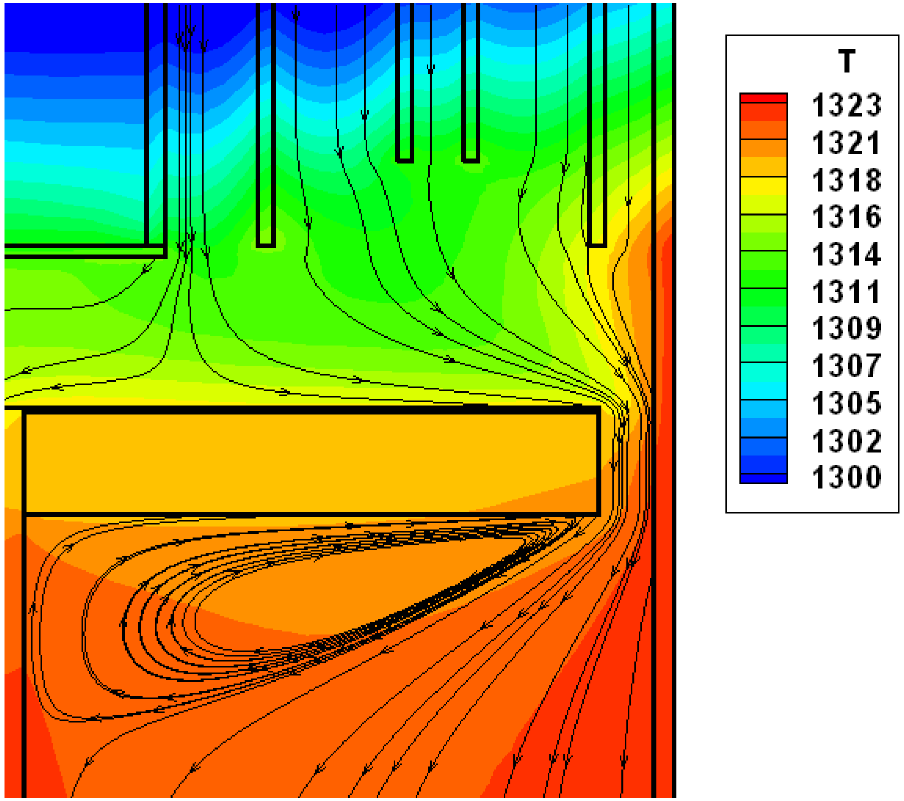
VR-HVPE
GaN/AlGaN/AlGaN

≡ HepiGaNs™ (Hydride Epitaxy GaN Simulator)



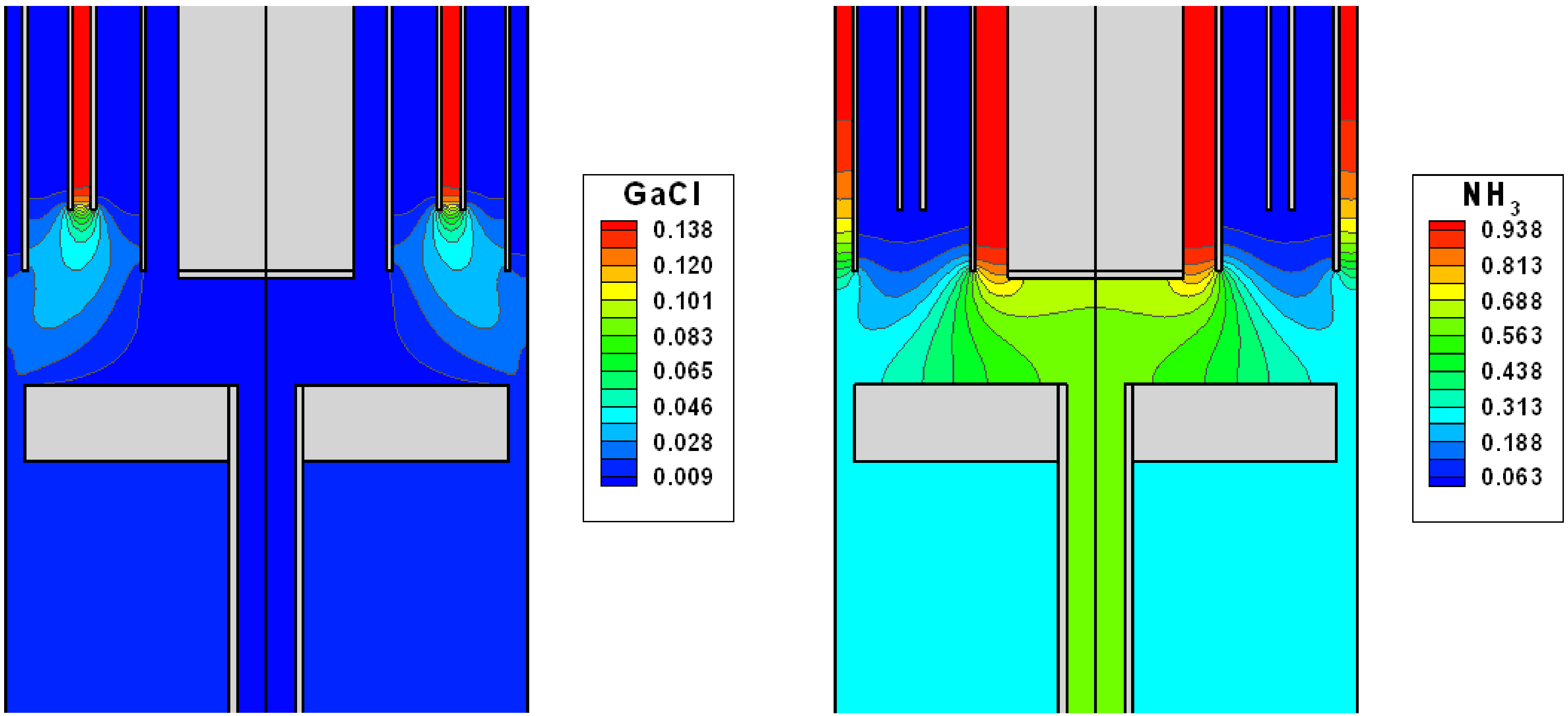
Gaseous species: NH_3, GaCl, HCl, H_2



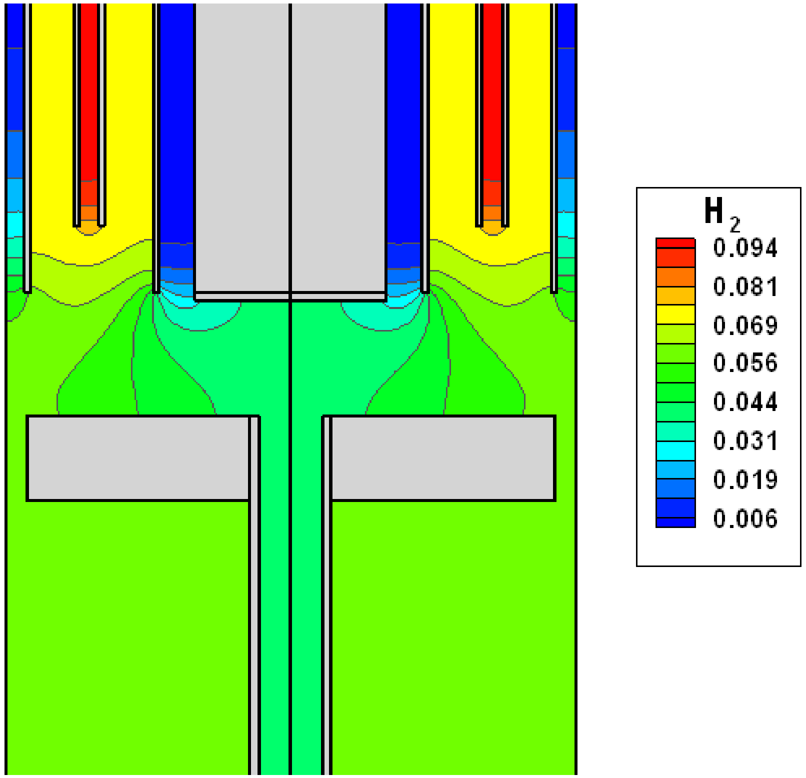


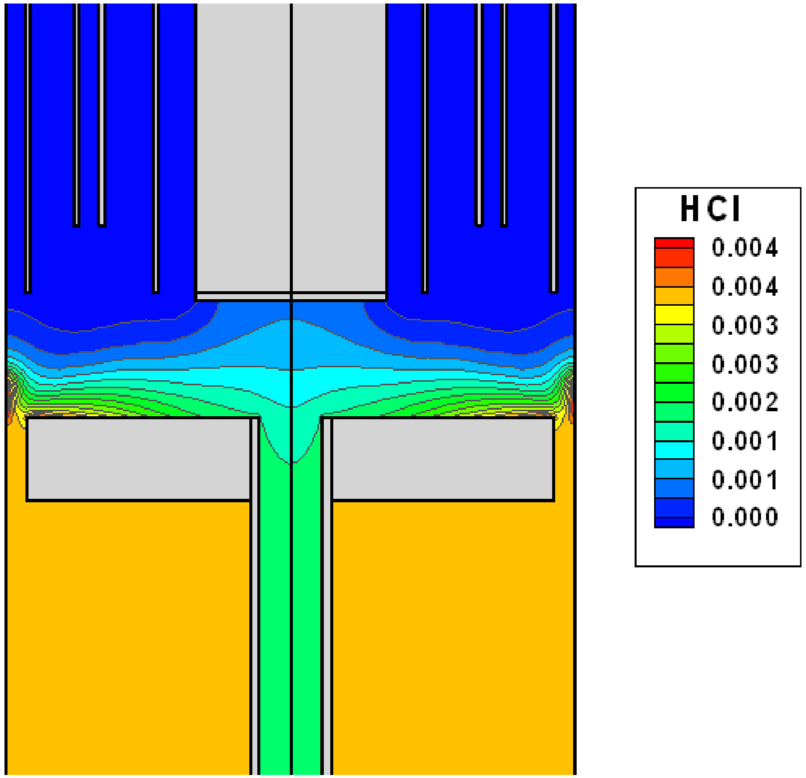
Flow pattern in the vicinity of the substrate

HEpiGaNS™ GaN Configuration: Mass Transport Modeling



Species Mass Fraction Distributions

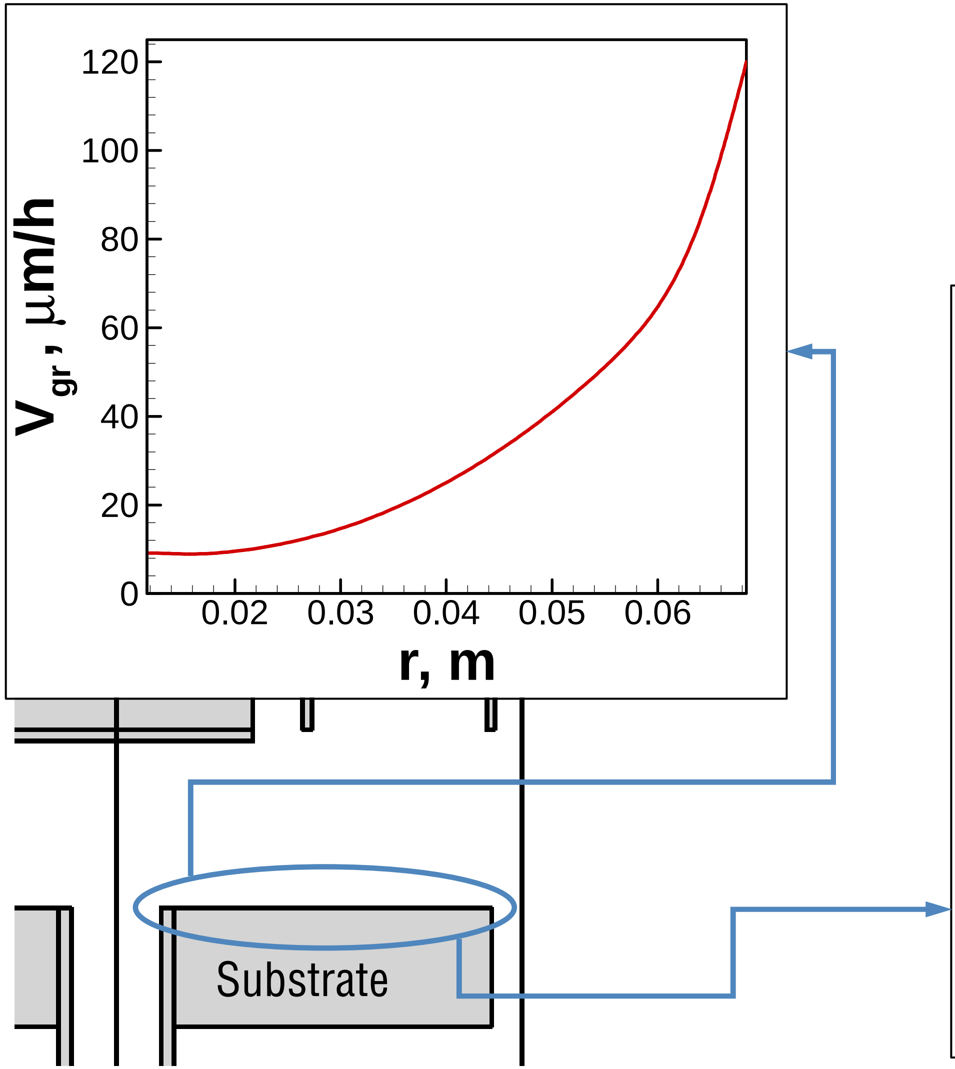


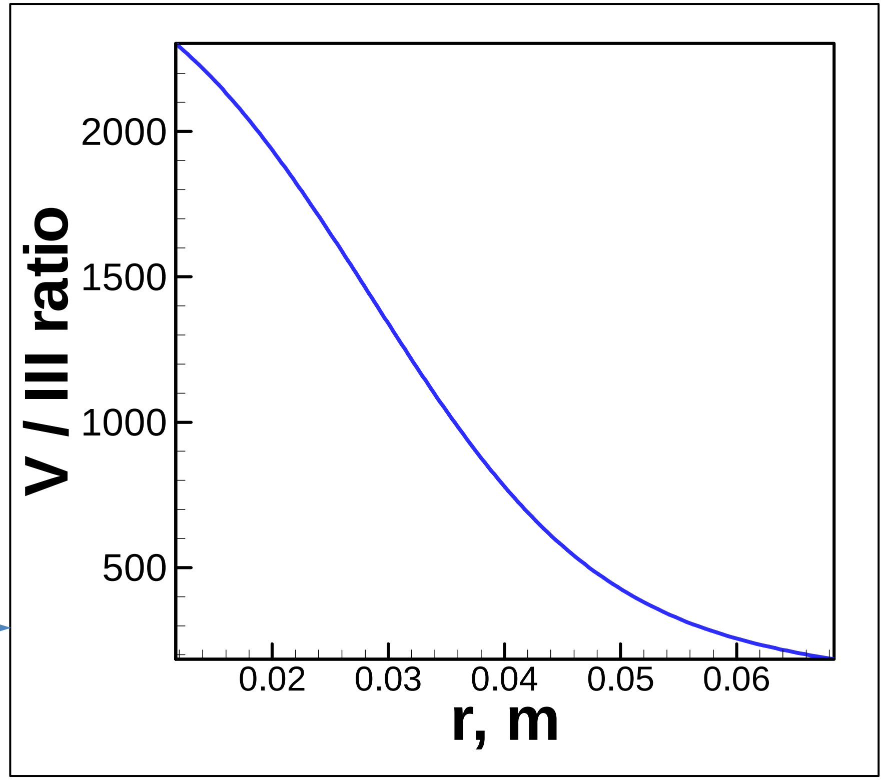


Species Mass Fraction Distributions

HEpiGaNS™ GaN Configuration: Mass Transport Modeling

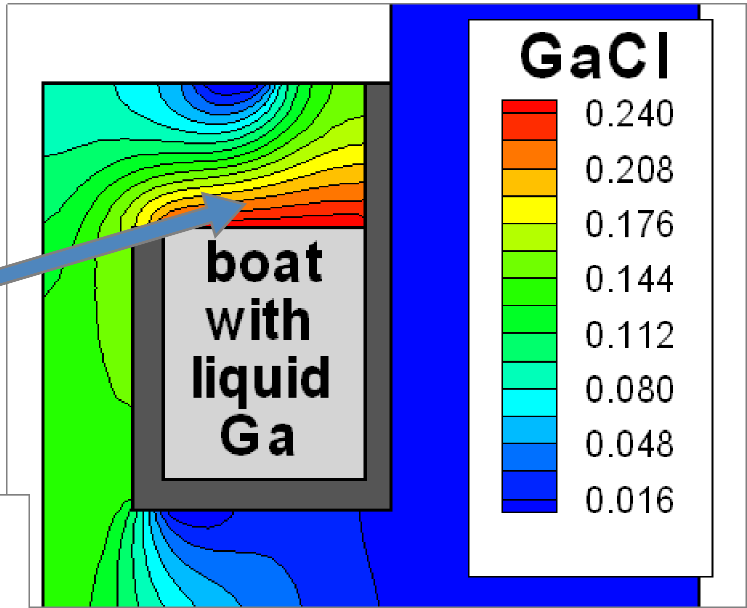
Growth rate and V/III ratio profiles along the substrate radius





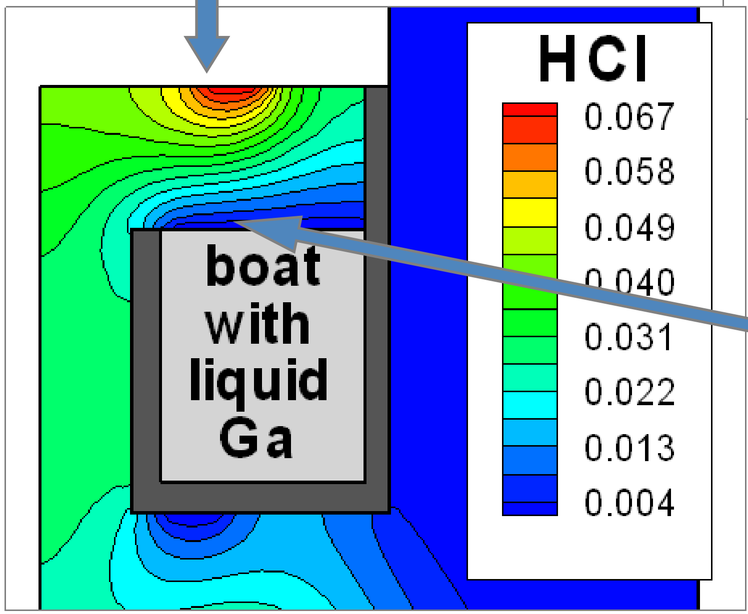
Ga Source Modeling

GaCl generation due to liquid Ga evaporation

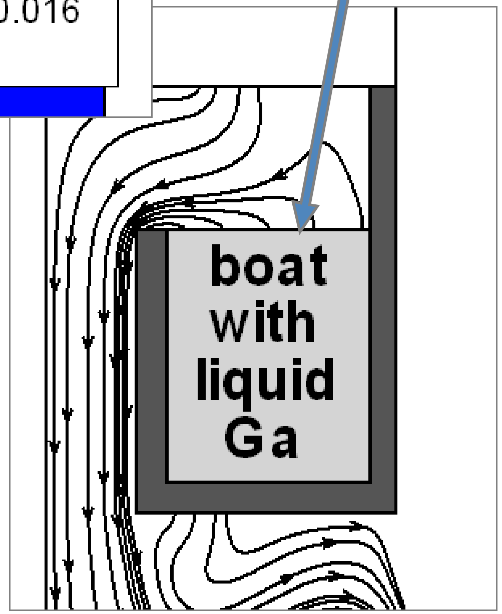


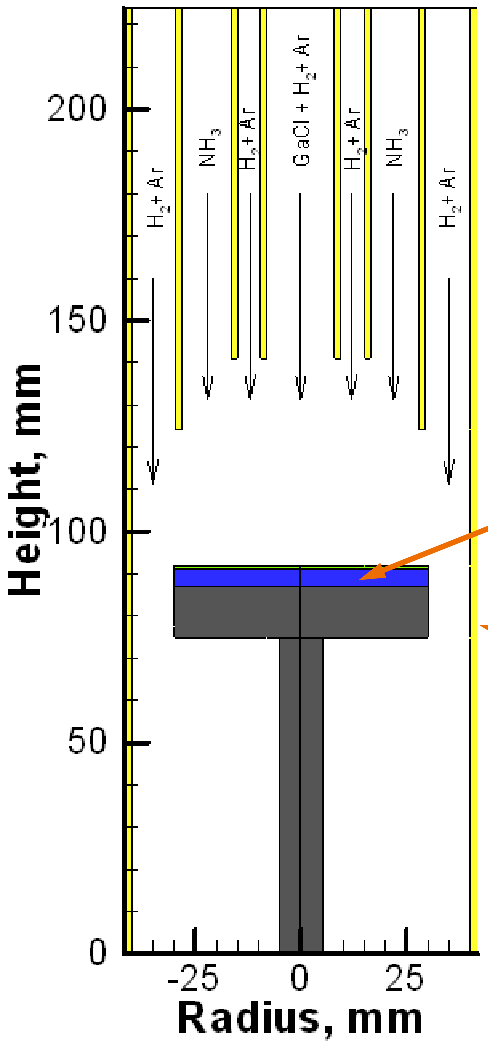
Liquid Ga evaporation

HCl supply



HCl consumption on the surface of liquid Ga

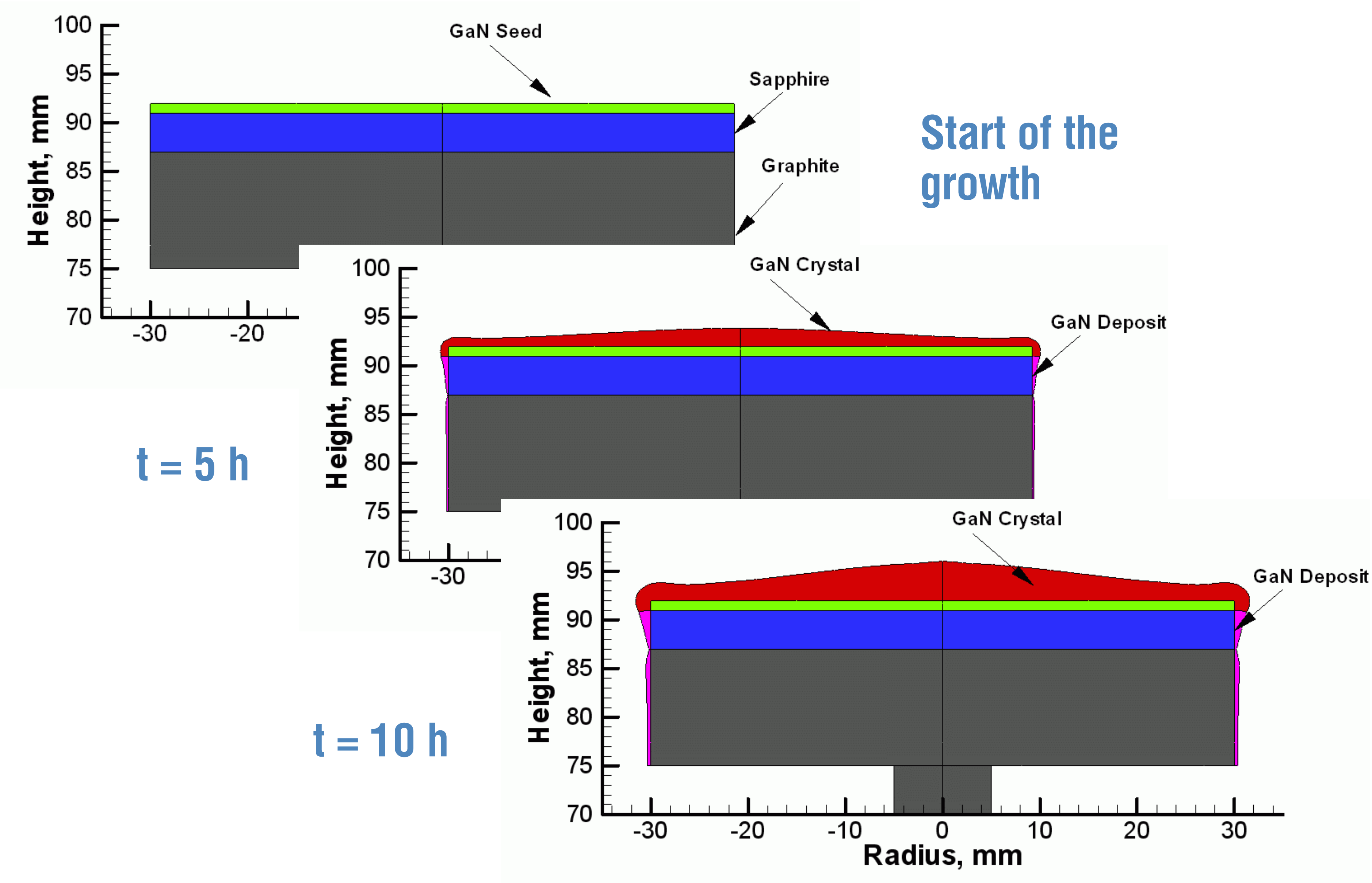




GaN deposition on the substrate

Parasitic GaN deposition

Crystal Shape Evolution

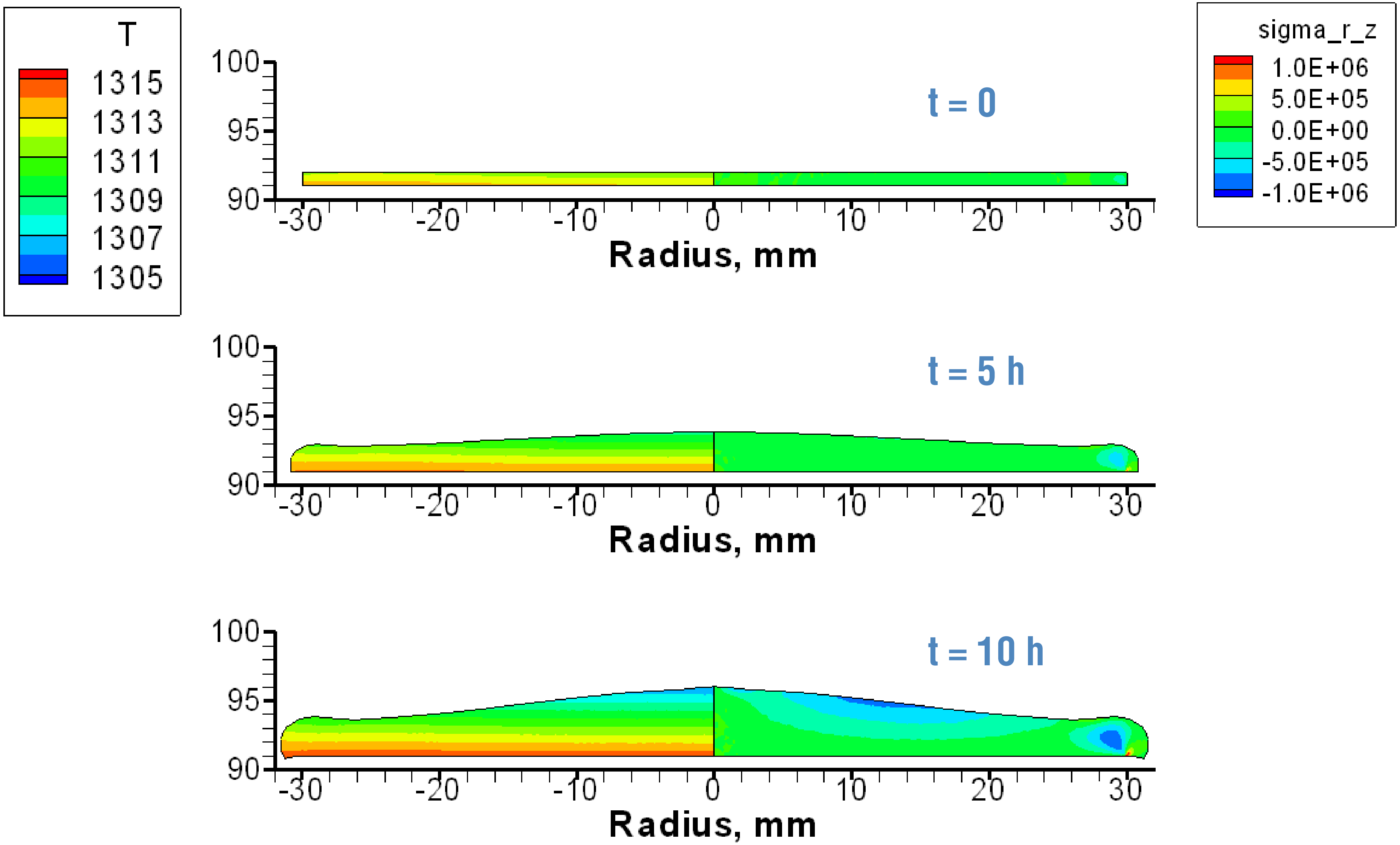


Start of the growth

t = 5 h

t = 10 h

Thermal Stress Evolution in the Growing Crystal



Virtual characterization: dislocation dynamics and crystal faceting

Basic Features

- **Finite-element analysis of the thermal elastic stress in hexagonal crystals**

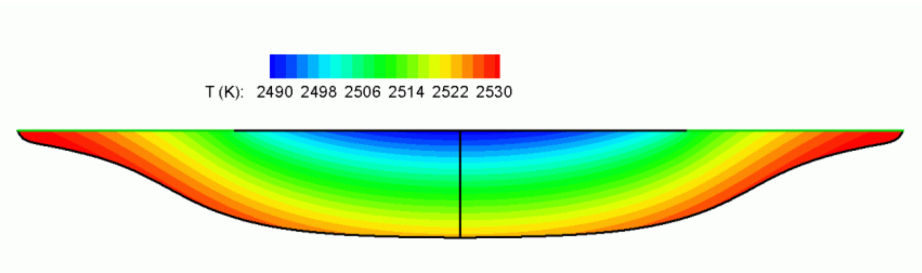
- **Anysotropic approach is applied**

- **Evaluation of the density of the dislocations gliding in the basal (0001) plane on the assumption of a full stress relaxation due to plastic deformation (S.Yu. Karpov et al., *J.Cryst. Growth* 211 (2000) 347)**

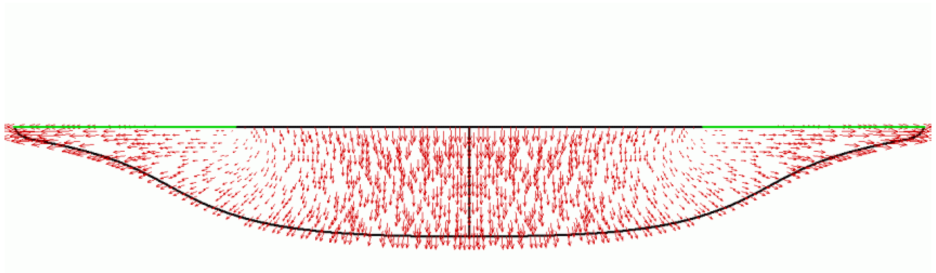
Stress analysis in SiC growth by PVT

t = 10 h

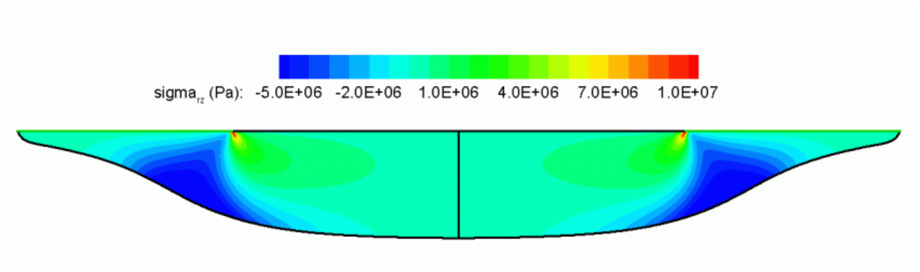
Temperature Distribution



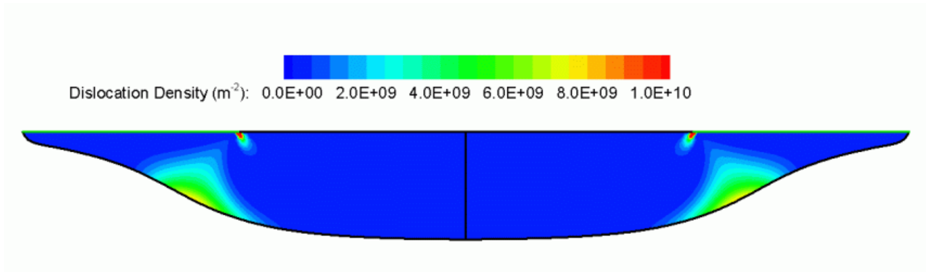
Displacement Vectors



σ_{rz} **Stress Component**

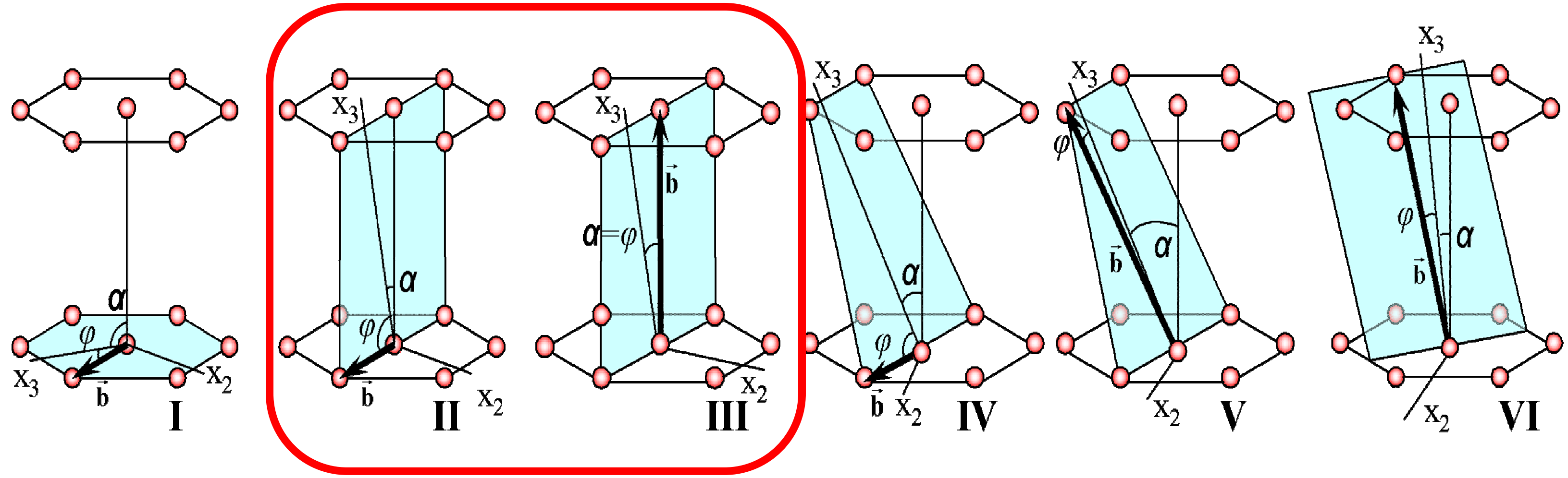


Dislocation Density Distribution



Boundary conditions: **Free** **Slip**

Principal Slip Systems in a Hexagonal Crystal



Virtual Reactor predicts propagation of dislocations of **II** (prismatic) and of **III** (screw) type frequently observed in the growing bulk crystal. The energetic approach was verified for modeling of dislocation behavior in thin layers and extended later for simulation of dislocation dynamics in bulk crystal growth.

I – $(0001)<1\bar{2}10>$

II – $\{10\bar{1}0\}<1\bar{2}10>$

III – $\{10\bar{1}0\}<0001>$

IV – $\{10\bar{1}1\}<1\bar{2}10>$

V – $\{10\bar{1}1\}<\bar{1}\bar{1}23>$

VI – $\{\bar{2}112\}<2\bar{1}\bar{1}3>$

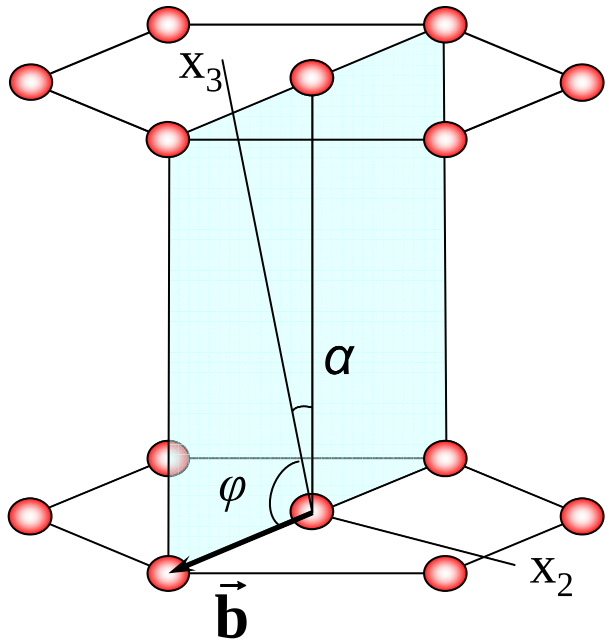
Energy of straight dislocation

$$E \sim K(\alpha)\cdot L\cdot \vec{b}^{\,2}$$

$K(\alpha)$ is the energy factor dependent on both the elastic constants of the material and the angle α of the dislocation inclination from the hexagonal axis of the crystal

$\vec{b}$ is the Burgers vector

L is the dislocation length



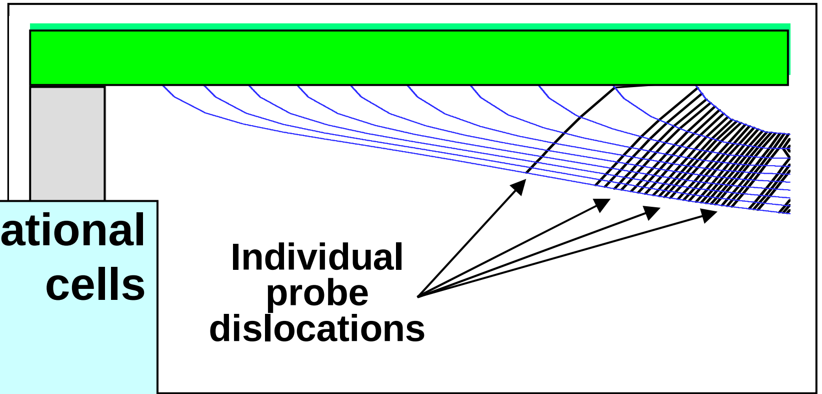
$$\alpha = (\overrightarrow{x_3}, <0001>)$$

$$\varphi = (\overrightarrow{x_3}, \vec{b}), \quad \alpha \propto \varphi$$

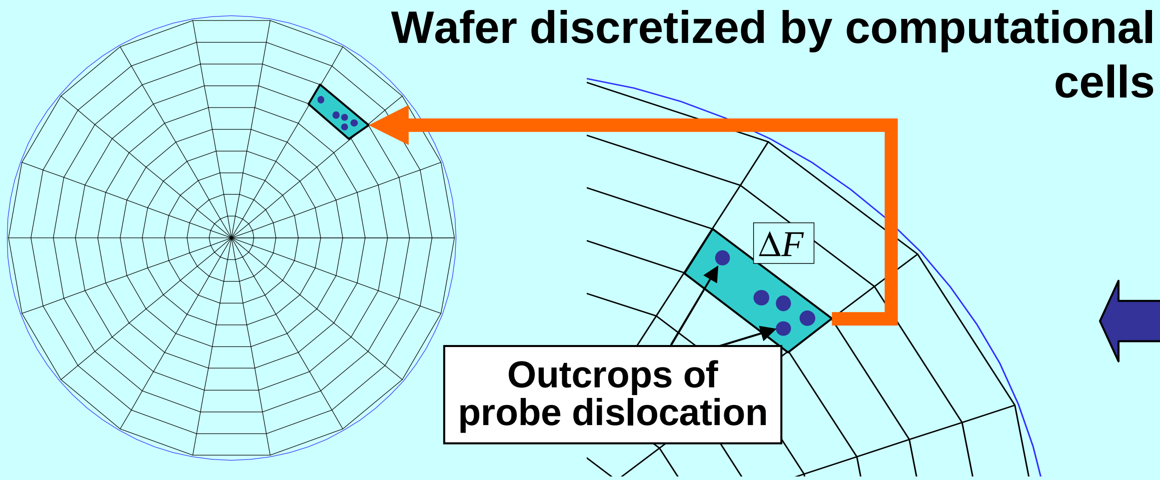
The developed approach operates with data on the crystal shape evolution, obtained numerically by Virtual Reactor

The analysis of Threading Dislocations (TD) evolution involves two options:

(i) TD trace tracking, providing interpretation of the dislocation lines in the growing bulk crystal

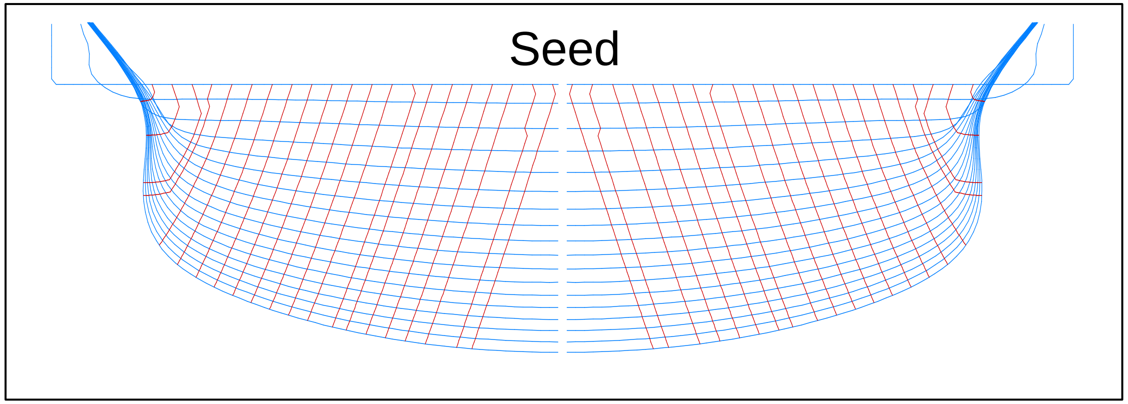


(ii) Virtual mapping, predicting the TD distribution in wafers cut from the crystal



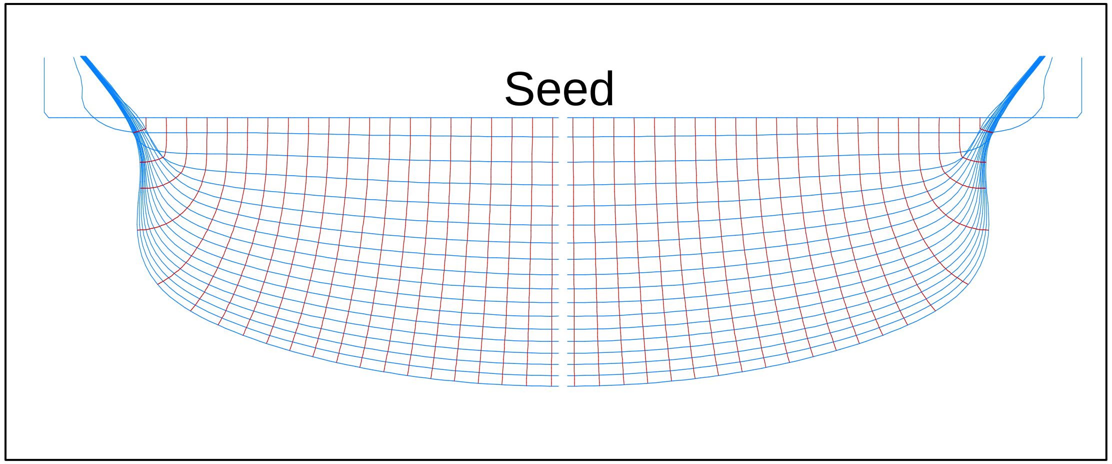
Dislocation density is computed as $n_k = N_k \cdot w_k / \Delta F$

Dislocation Traces in a Bulk SiC Crystal Growth



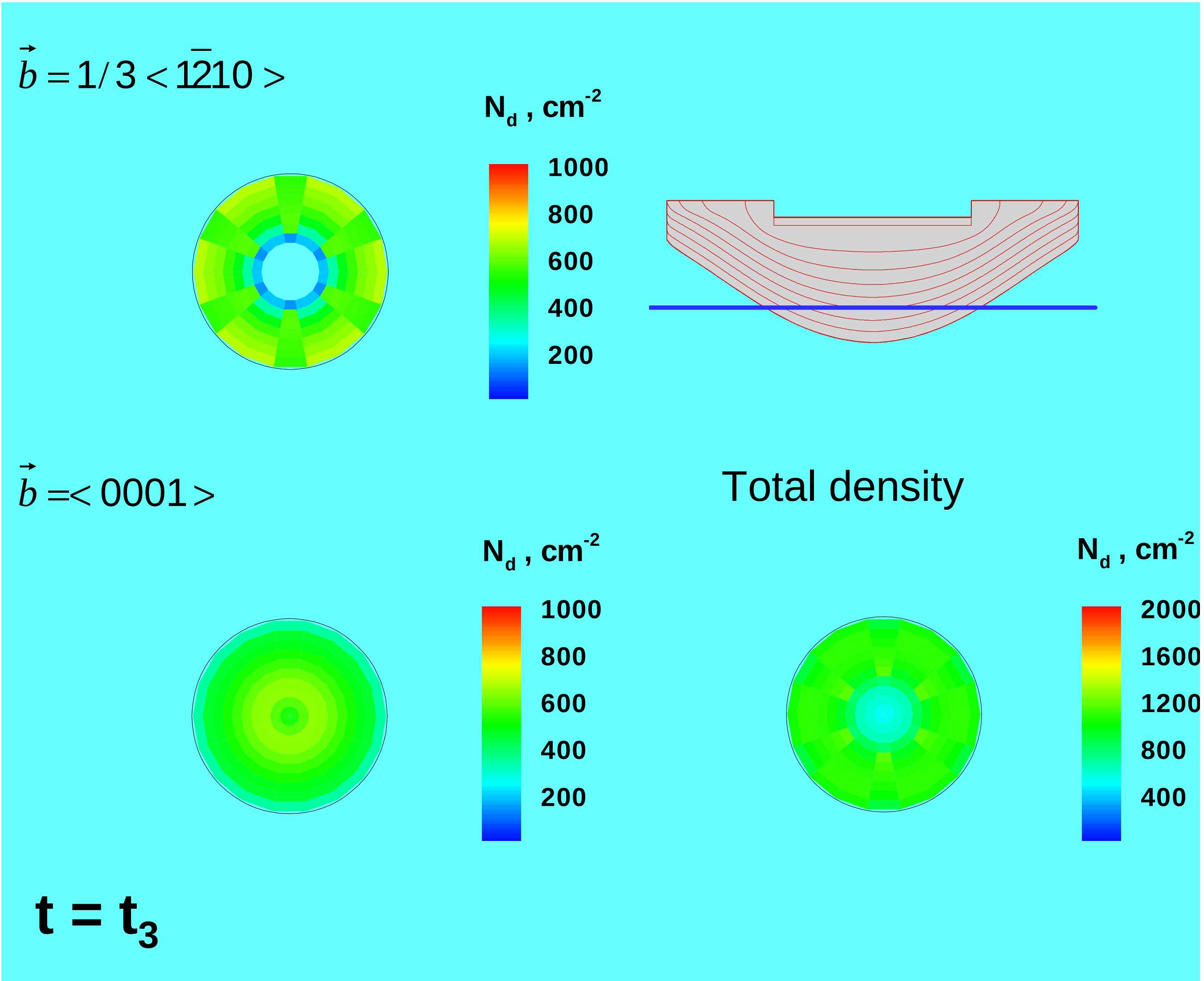
Slip System II:

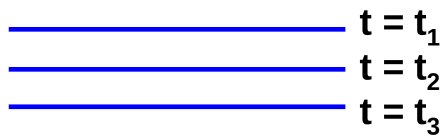
$$\{10\bar{1}0\} < 1\bar{2}10 >$$

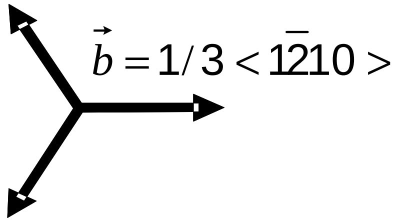


Slip system III:

$$\{10\bar{1}0\} < 0001 >$$





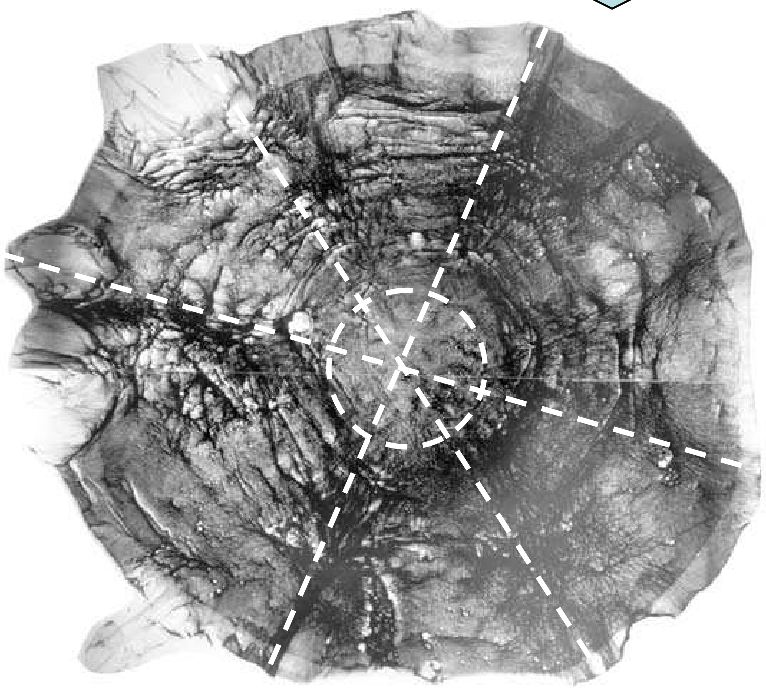


4H-SiC

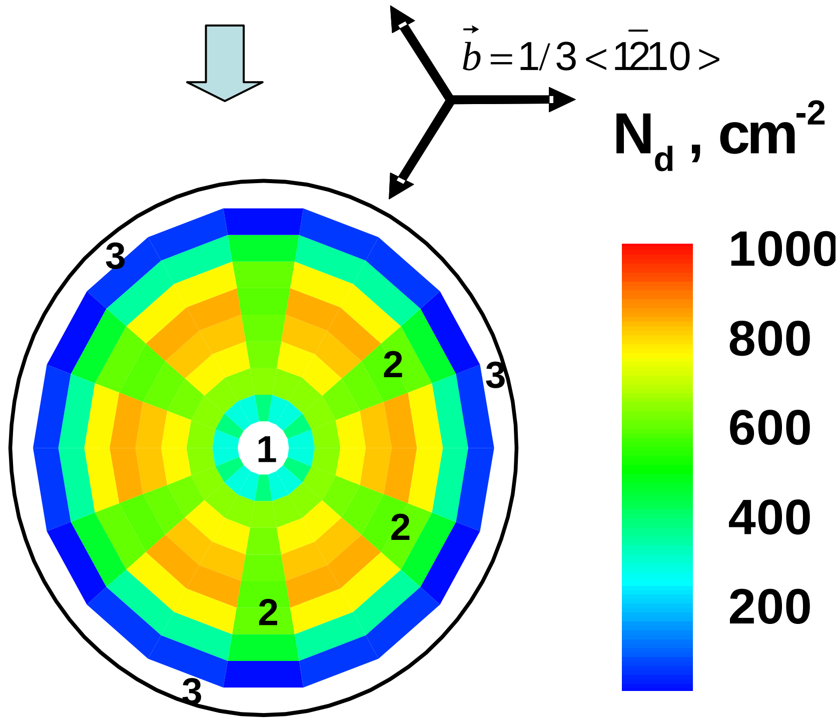
$N_p = 50 \cdot 10^3$

Virtual Mapping: TD distribution over the wafer surface

Synchrotron back reflection topography image of a typical 6H-SiC wafer (by E.A. Preble et al., J. Cryst. Gr. 2003)



Predicted distribution of $\{10\bar{1}0\} < 1\bar{2}10 >$ TDs over the wafer surface

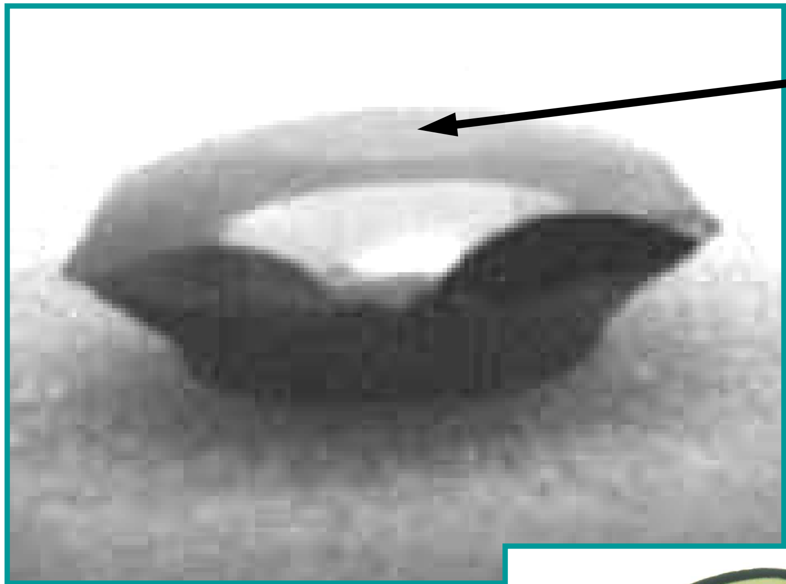


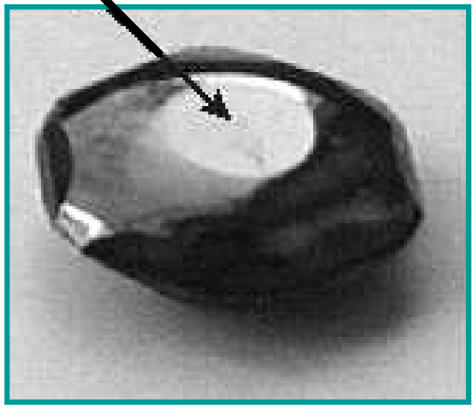
Several areas observed experimentally were identified numerically

- **Central area of reduced dislocation density**
- **Sectors with reduced dislocation density**
- **Marginal dislocation-free region**

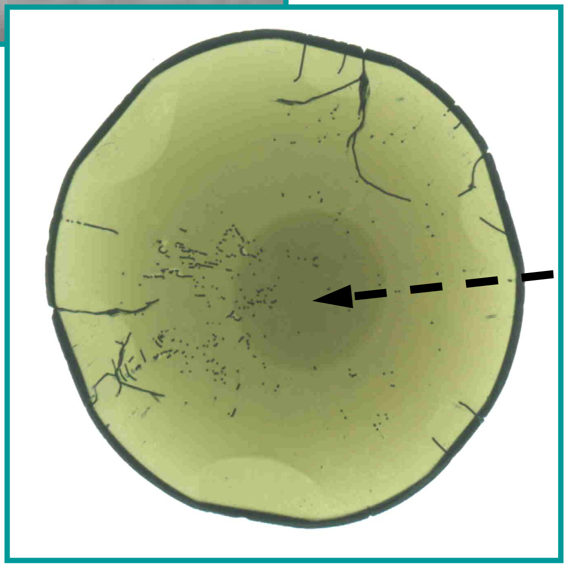
{0001}

Free-spreading SiC crystals usually grow with a pronounced hexagonal shape





Facet heavy doped by nitrogen

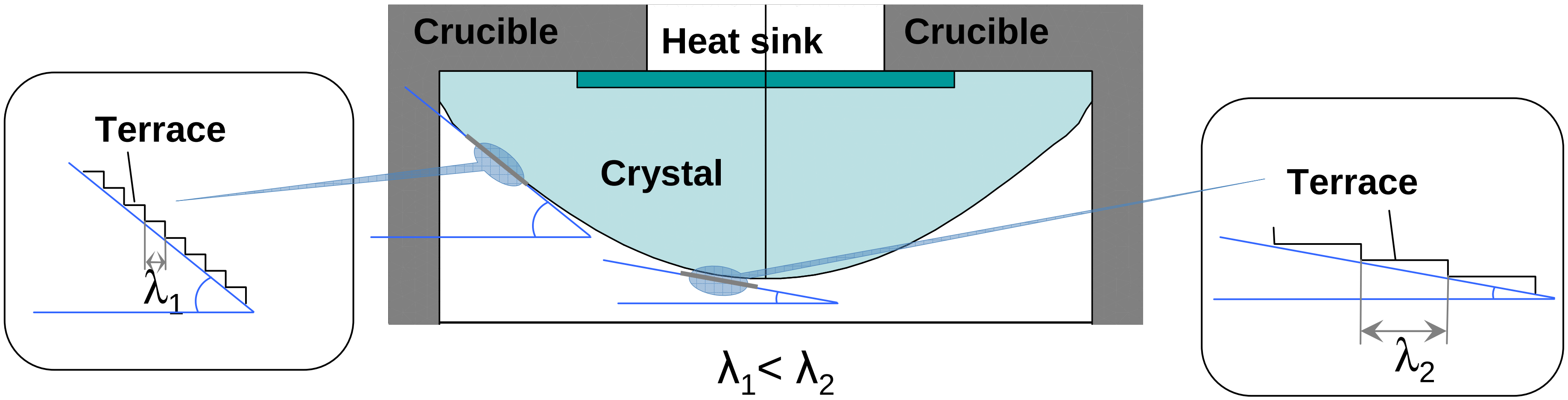


Slice of 30 mm in diameter SiC crystal etched in KOH for more than 1 h @ 500 ^{o}C

Jointly with Crystal Growth Science and Technology Laboratory, Russia

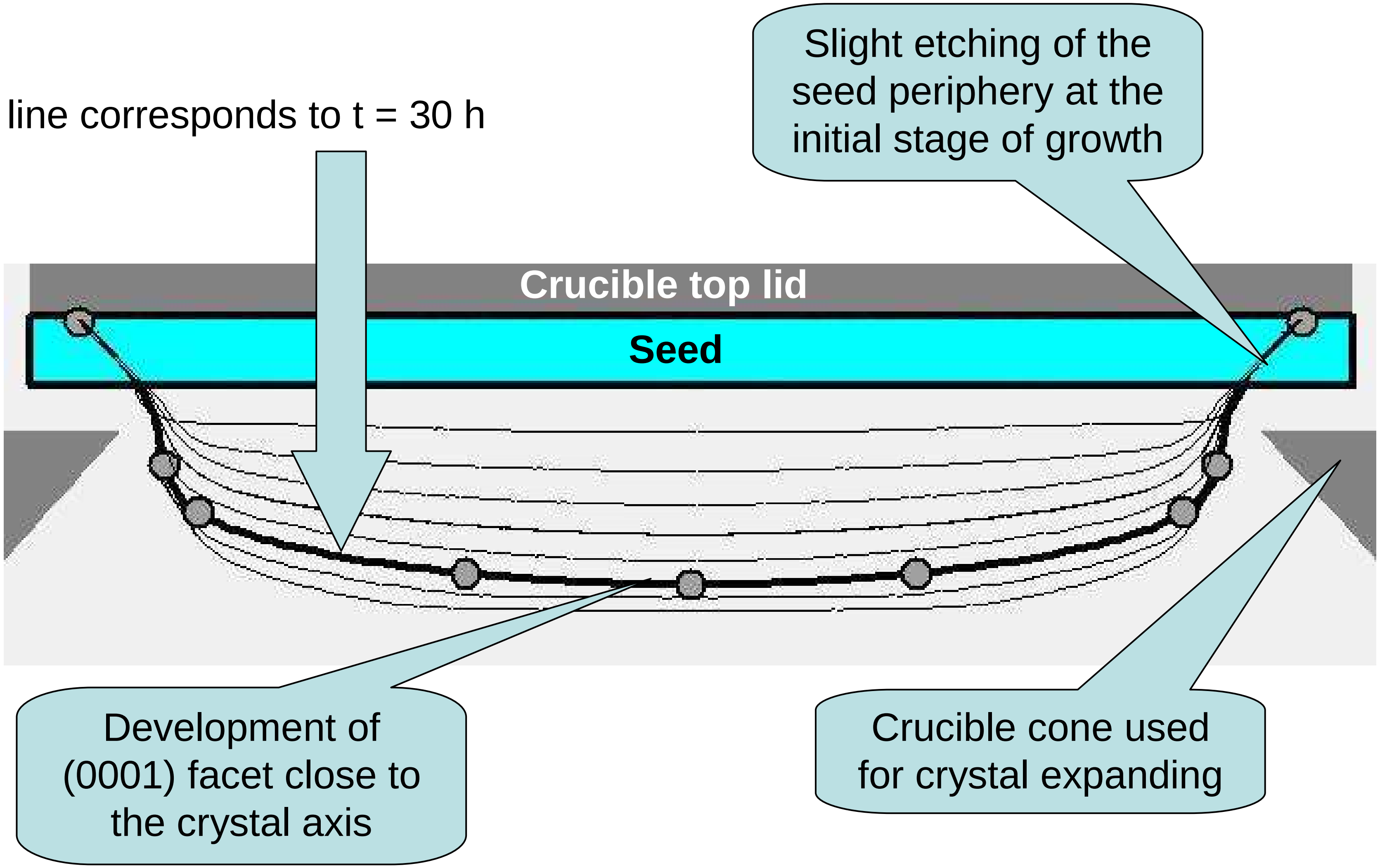
Basic Assumptions

- Step-flow growth mechanism model based on BCF approach
- Surface diffusion over a terrace is limiting process
- Local growth rate depends on terrace width λ
- Terrace width λ depends on local orientation angle



The distance between consecutive profiles is 5h

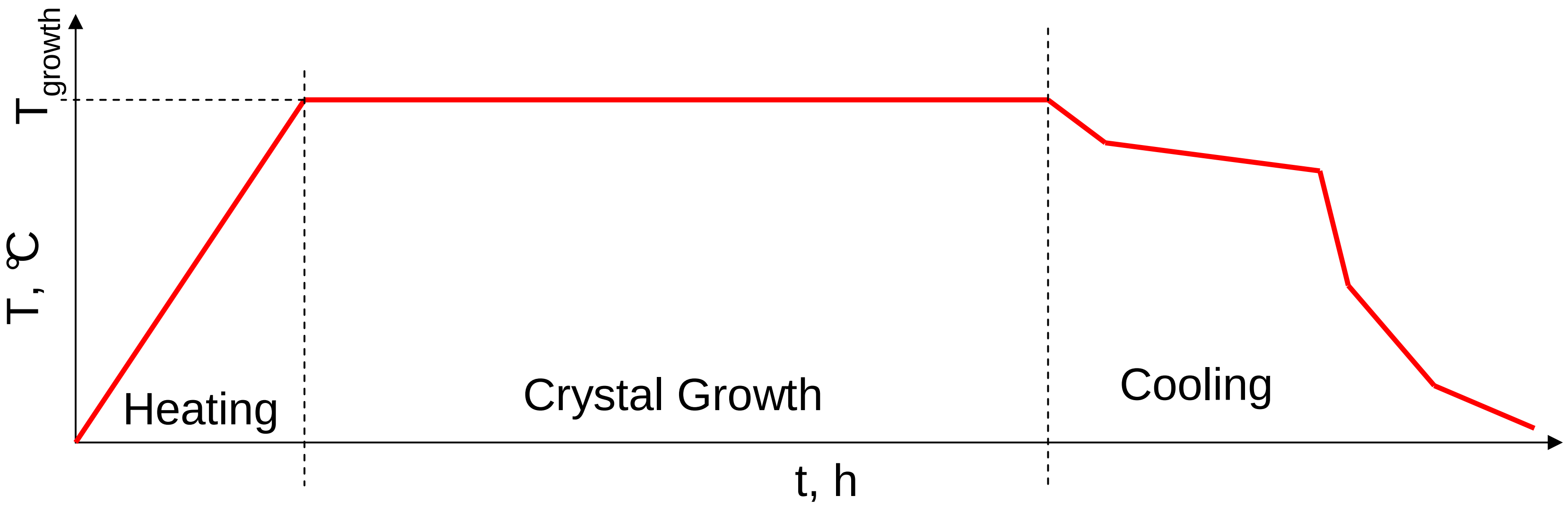
Bold line corresponds to t = 30 h



Unsteady Module

Key Features

- Unsteady heating of the growth system before the crystal growth
- Unsteady cooling of the growth system after the crystal growth
- Support of user-defined specification of both variation of the heater power and temperature at the reference point
- Thermal stress in the grown crystal during the cooling accounting for crystal plasticity



Unsteady Module

Temperature variation according to the user defined profile of power or temperature increase

→

Basic Virtual Reactor

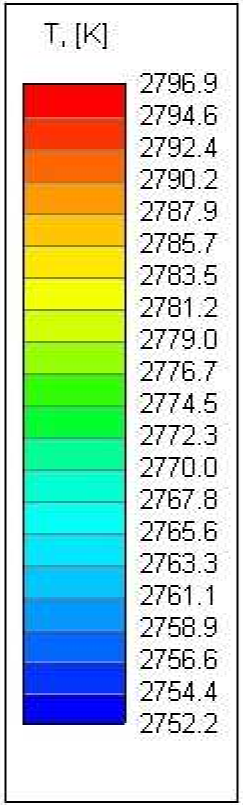
Solution of the heat and mass transport with crystal shape evolution

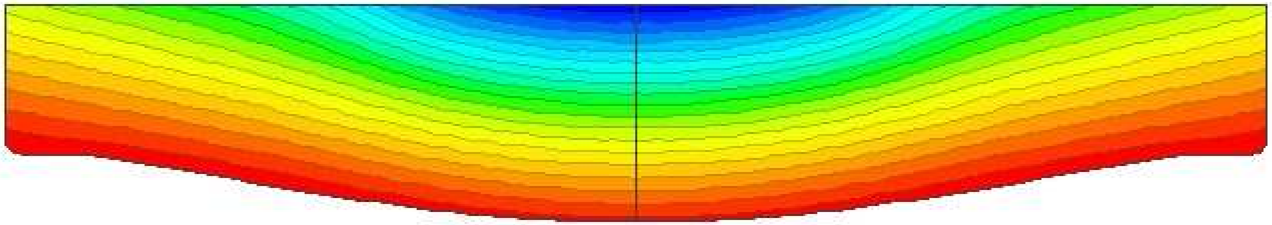
→

Unsteady Module

Temperature and thermal stress variation according to the user defined profile of power or temperature decrease

Examples of Computation: Thermal Stress





Temperature distribution at the start of the cooling stage = Initial T_{ref} distribution

Effect of embrittlement at a certain temperature equal to Tembr:

- at $T>T_{embr}$ crystal is plastic
- at $T<T_{embr}$ crystal is brittle

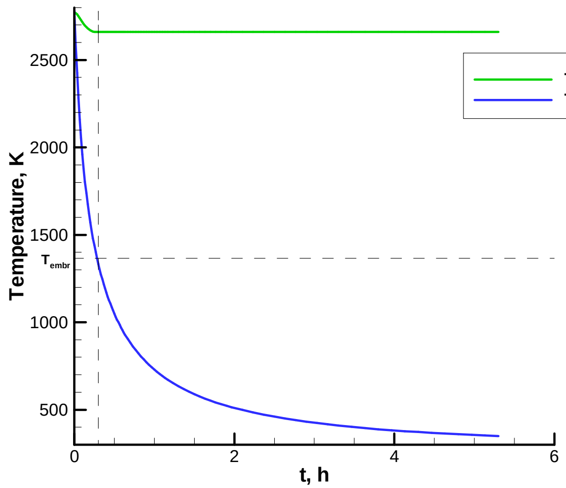
$$\sigma_{ii} = \sum_j C_{ij}\left(\varepsilon_{jj} - \alpha\left(T - T_{ref}\right)\right)$$

$$\frac{dT_{ref}}{dt} = -\frac{1}{\tau(t)}\left(T_{ref} - T(t)\right)$$

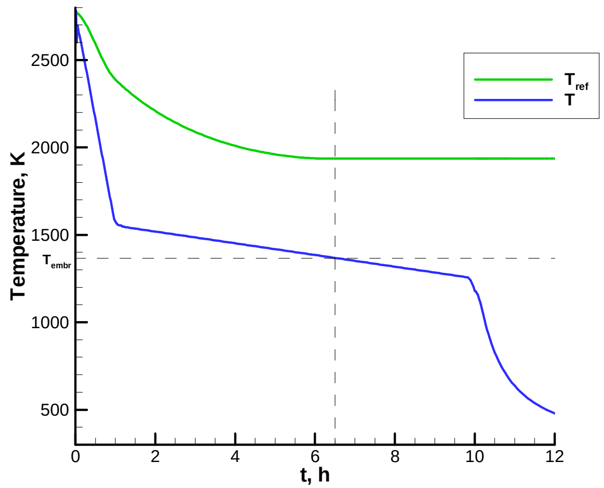
If T_{ref} does not relax, $T-T_{ref}$ is high and one can expect high value of stress at room temperature

Examples of Computation: Thermal Stress

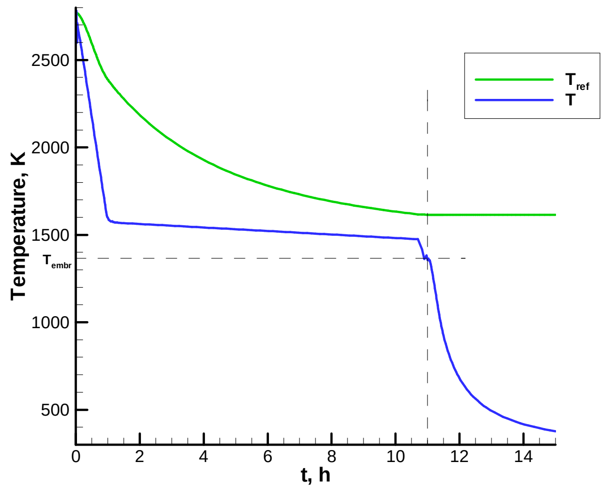
Reduction of the average temperature over the crystal (T) and the reference temperature T_{ref} at different



Rapid Cooling



Medium Cooling

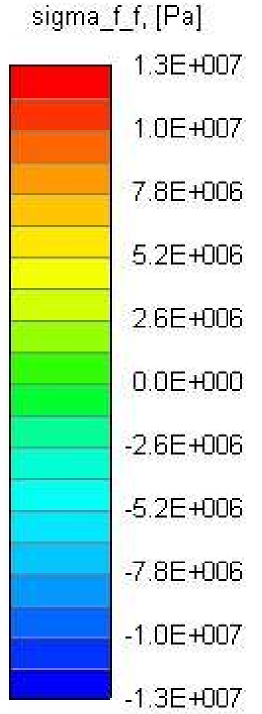


Slow Cooling

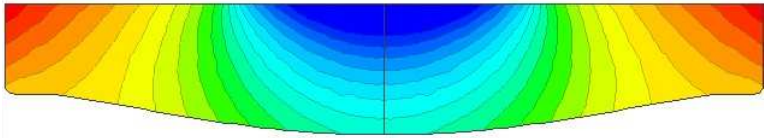
Power is switched off at once: $Q(t>0) = 0$

In the temperature range before $T = T_{embr}$, heater power drops slowly to reduce the temperature decrease rate

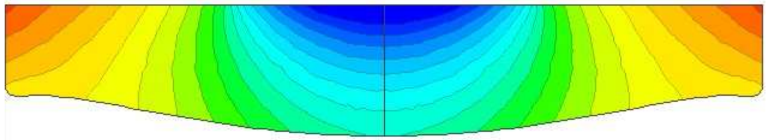
Evolution of Thermal Stress responsible for crystal cracking



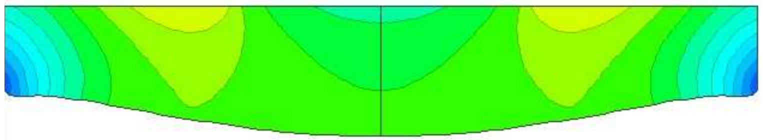
Distribution of the $\sigma_{\varphi\varphi}$ stress tensor component at different cooling recipes



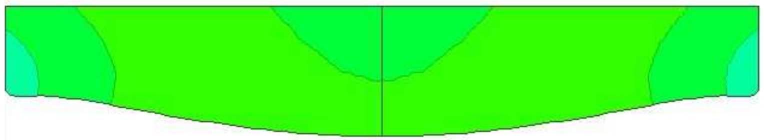
No Relaxation



Relaxation at Rapid Cooling



Relaxation at Medium Cooling

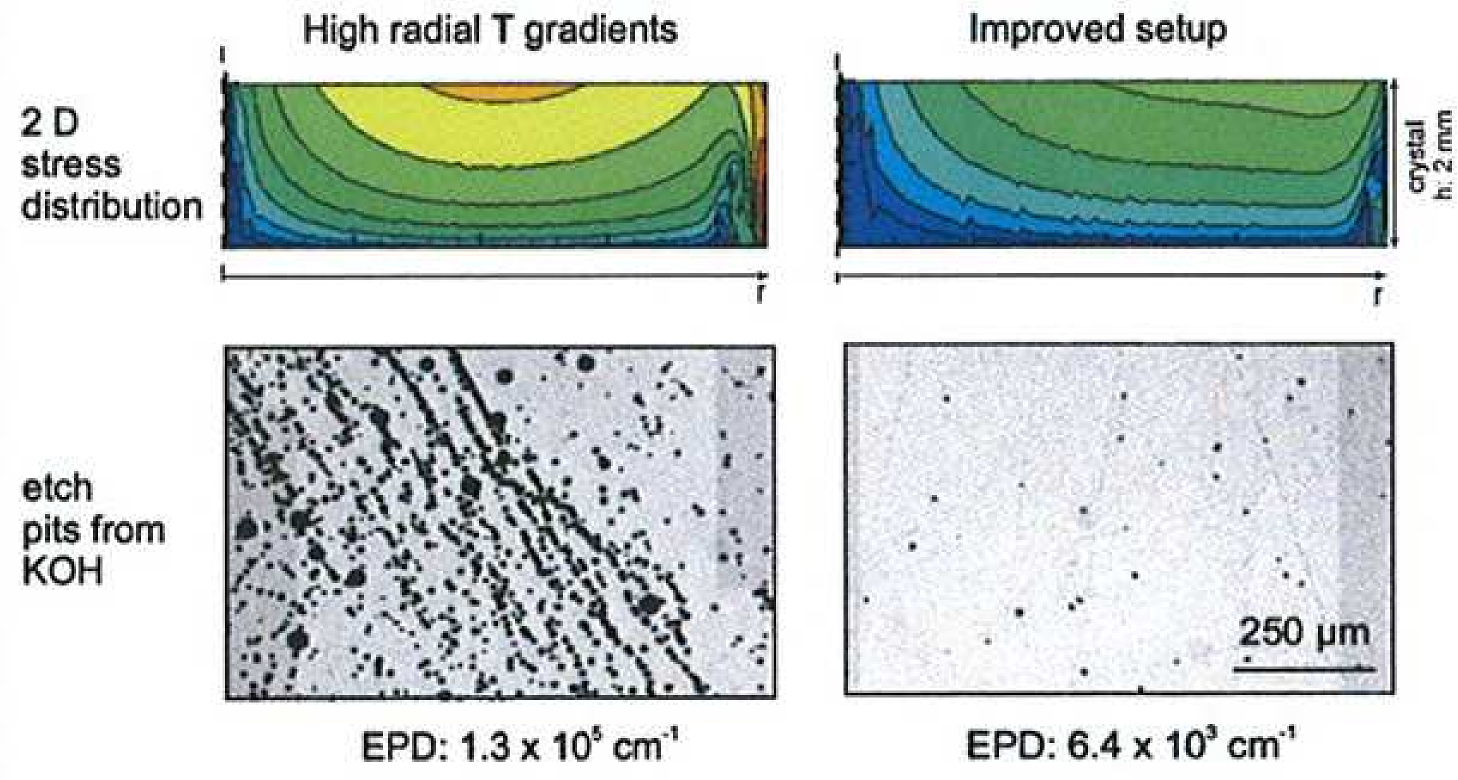


Relaxation at Slow Cooling

High positive values of the $\sigma_{\varphi\varphi}$ stress tensor component are attributed to cause radial crystal cracking, so control of $\sigma_{\varphi\varphi}$ is beneficial to provide high quality crystals

Virtual Reactor Success Stories

Thermoelastic Stress predicted by VR simulations and EPD measured experimentally

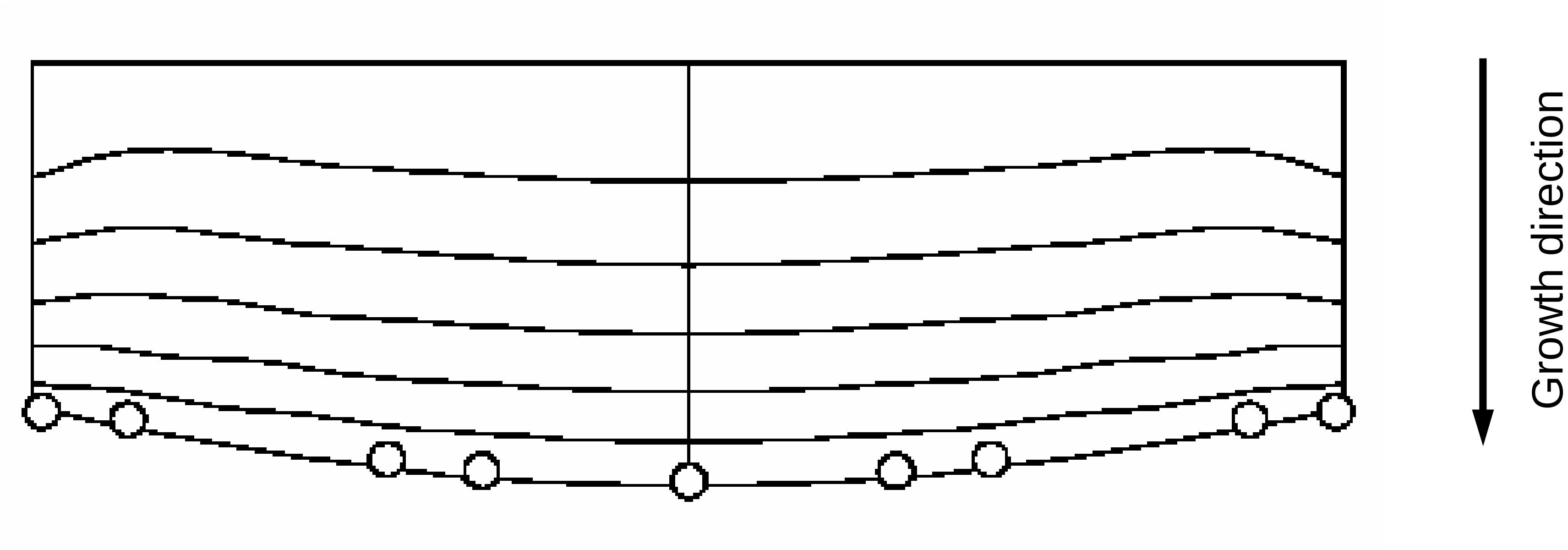


Reduction of BPD and TED achieved by improved thermal conditions.

ICSCRM2007
MoP-32
E. Schmitt et al.

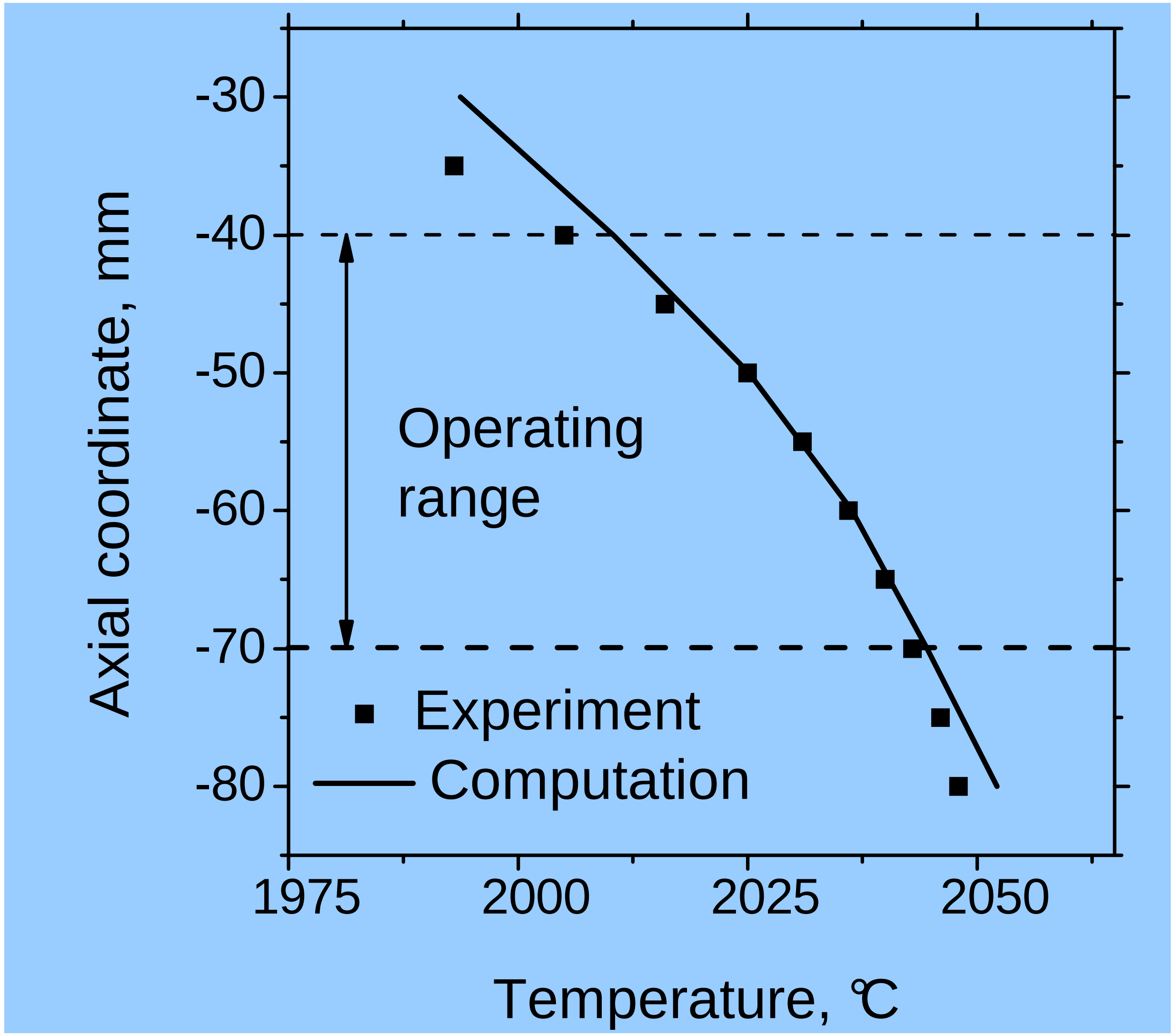
SiCrystal AG, Germany

- Computer simulations and growth experiments were performed
- Several methods for the evaluation of material properties were applied to get a better understanding of defect generation like polytype inclusions and SFs



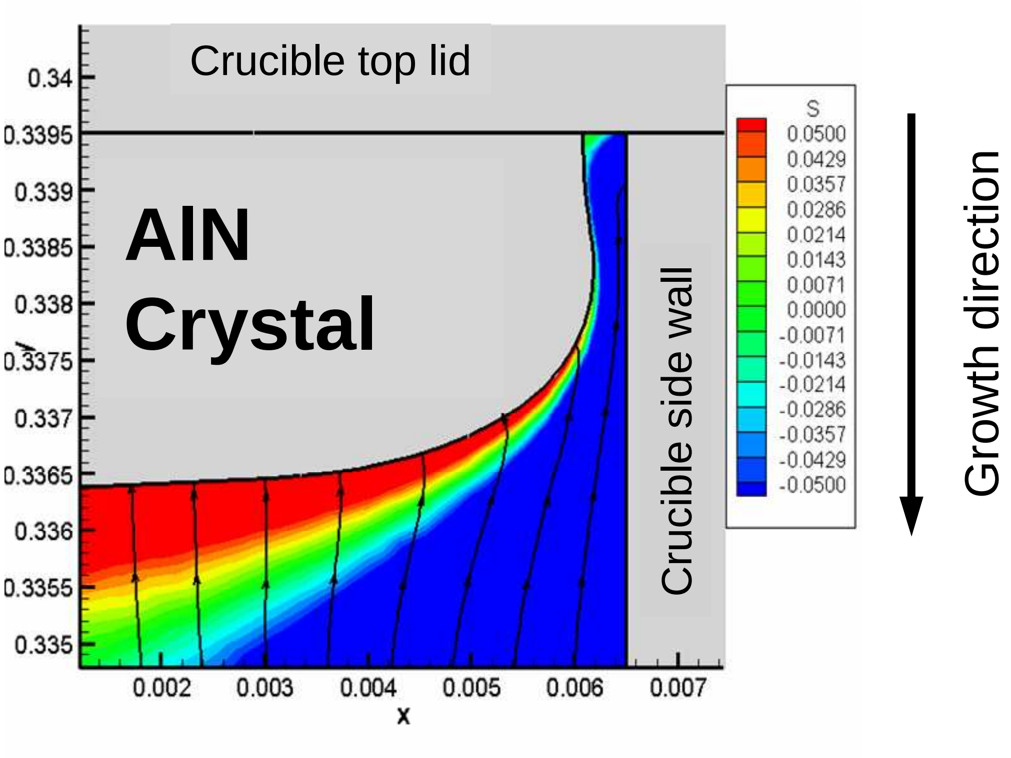
SiC boule evolution. The growth front shape is shown with an interval of 10 h

Galyukov et al. (2007) ICSCRM2007, WeP-25



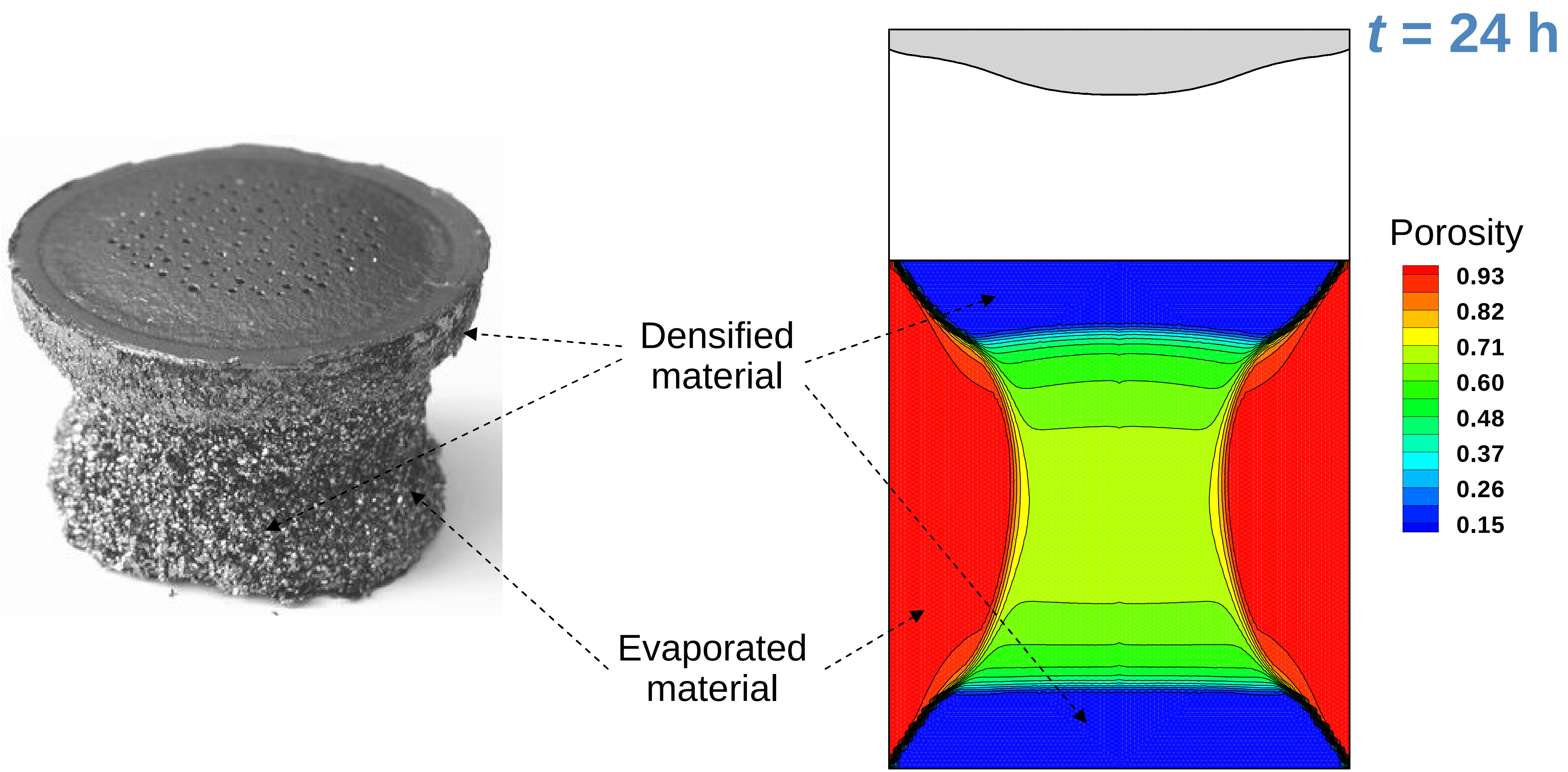
Temperature at the center of the crucible lid vs. its location at the vertical axis – comparison of the results of computations with ViR-PVT AlN™ and pyrometric measurements

Simulation



Experiment

Shape of the PVT grown bulk AlN crystal: comparison of the results of computations with ViR-AlN PVT™ and really grown crystal (the left figure displays also the computed supersaturation map and streamline pattern)



Porosity distribution in the SiC powder source

M. Bogdanov et al. (2003)

ELSEVIER

Available online at www.sciencedirect.com
SCIENCE DIRECT

Journal of Crystal Growth 275 (2005) e1807–e1812

JOURNAL OF CRYSTAL GROWTH
www.elsevier.com/locate/jcrysgro

In situ visualization of SiC physical vapor transport crystal growth

Peter Wellmann[a,*], Ziad Herro[a], Albrecht Winnacker[a], Roland Püsche[b], Martin Hundhausen[b], Pierre Masri[c], Alexey Kulik[d], Maxim Bogdanov[d], Sergey Karpov[d], Mark Ramm[d], Yuri Makarov[e]

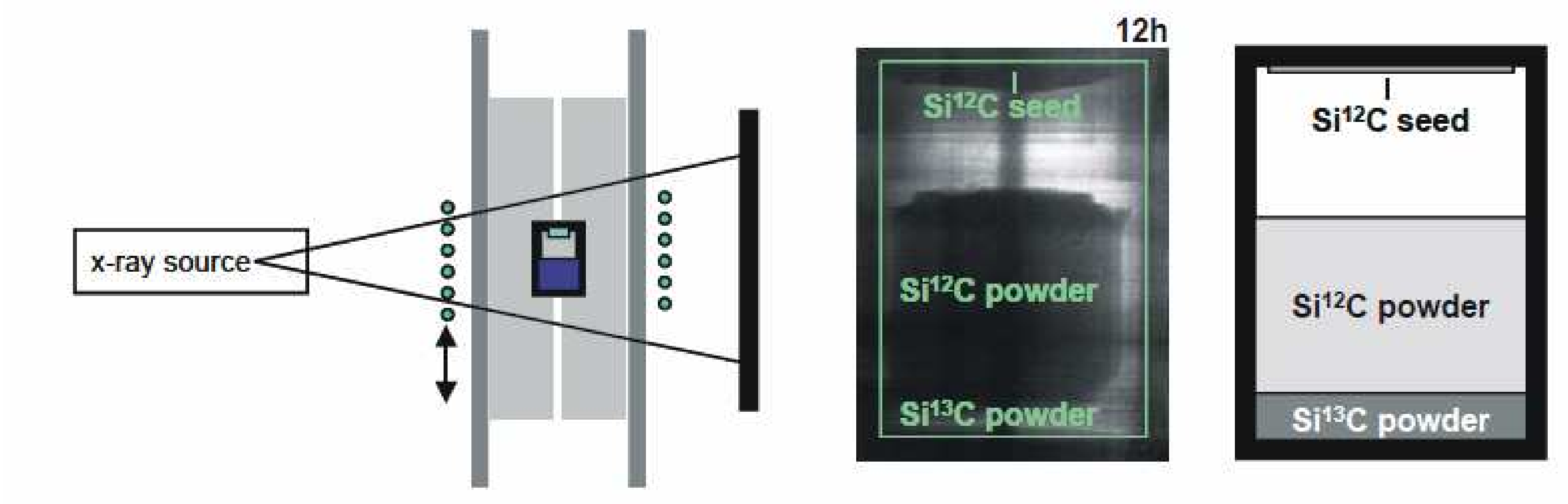


Fig. (Left) Sketch of the digital X-ray imaging setup for in situ monitoring of the SiC crystal growth process. (Center) Typical X-ray image showing the SiC crystal as well as the SiC source material with its morphology after 12 h of growth. (Right) Detailed sketch of the growth cell; in the bottom area the location of the $Si^{13}C$ charge for the ^{13}C-labeling experiment is pointed out.

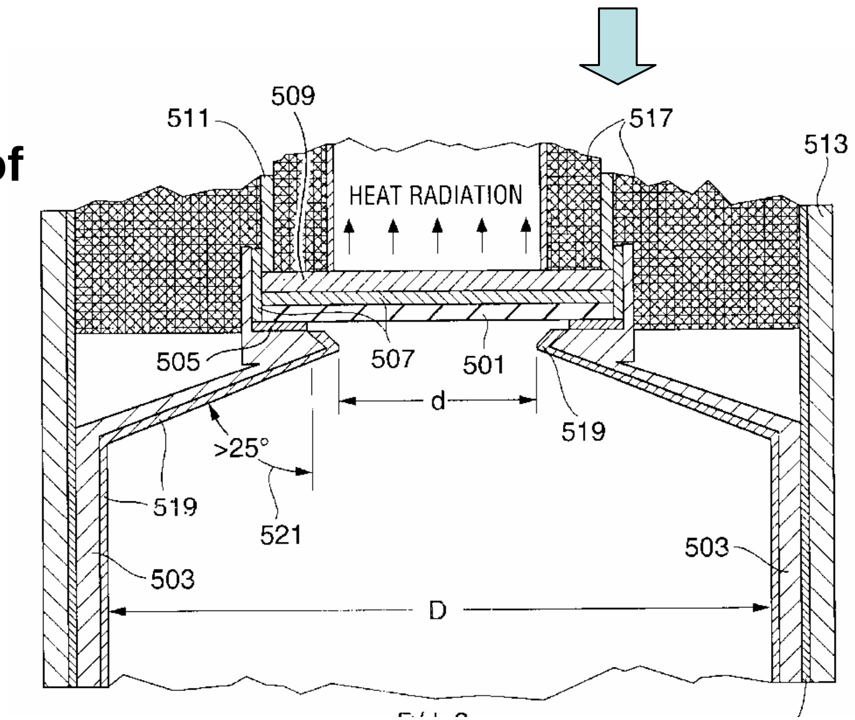
New technique development: lateral growth plus carbonized Ta

Growth of Low-Defect SiC Bulk Crystals by Sublimation

To grow SiC crystal with as large as possible areas free of macroscopic defects (micropipes, dislocations, cracks, etc.) the advanced growth technique was developed

Key Features

- **Enhanced lateral growth at early stage of the process. Laterally grown SiC can be free of macroscopic defects**
- **Use of carbonized Ta as container material**



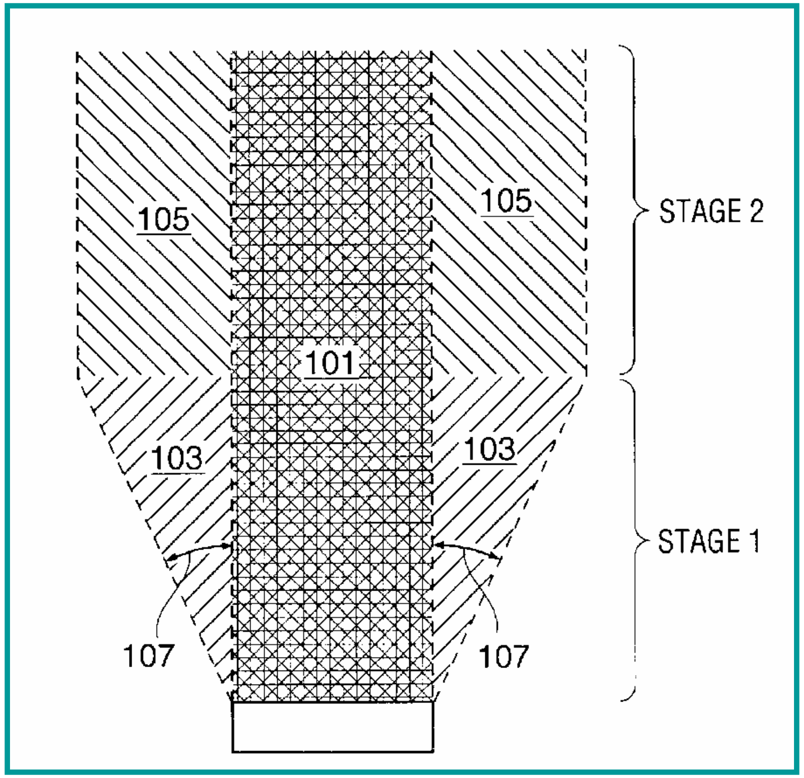
Jointly with Crystal Growth Science and Technology Laboratory, Russia

First stage

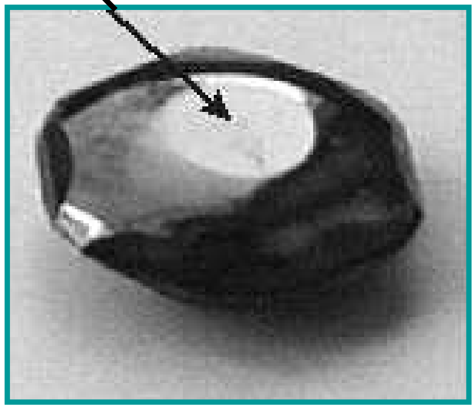
Crystal is growing in normal direction and expanding laterally: $V_{lateral}/V_{axial}=0.35÷1.75$ ($22-70^{o}$)

Second stage

Lateral growth is suppressed, and normal growth is enhanced: $V_{lateral}/V_{axial}=0.1÷0.3$



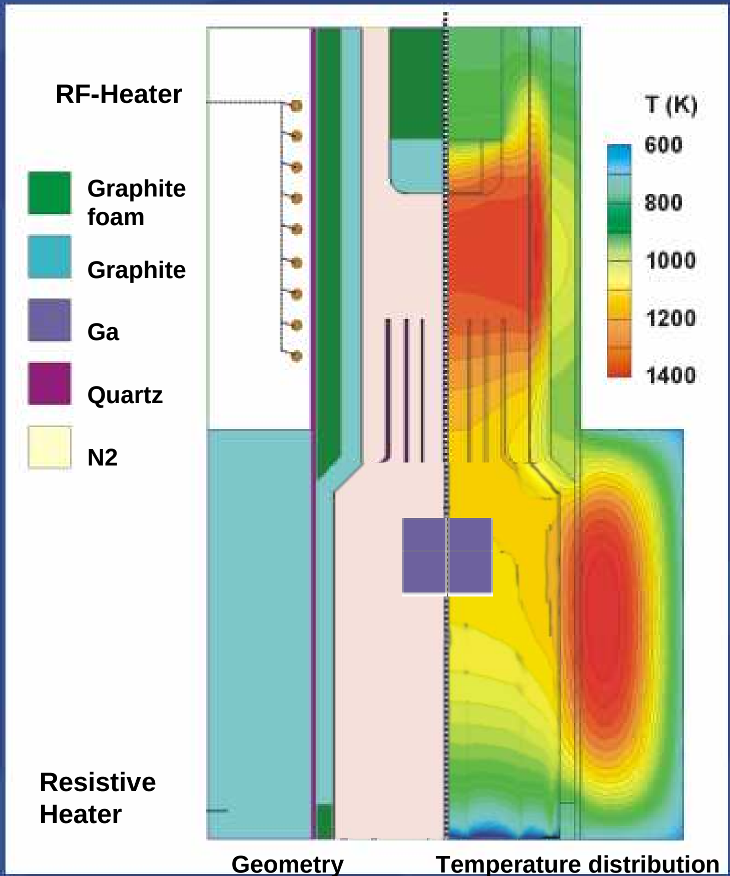
Free-spreading SiC crystals usually grow with a pronounced hexagonal shape



Yu.A. Vodakov et al. U.S. Patent N 6,562,131, U.S. Patent N 6,562,130, N 6,547,877, N 6,537,371, U.S. Patent N 6,534,026, U.S. Patent N 6,508,880 (2003)

S. Hagedorn et al., DGKK Marburg 2007

Simulation



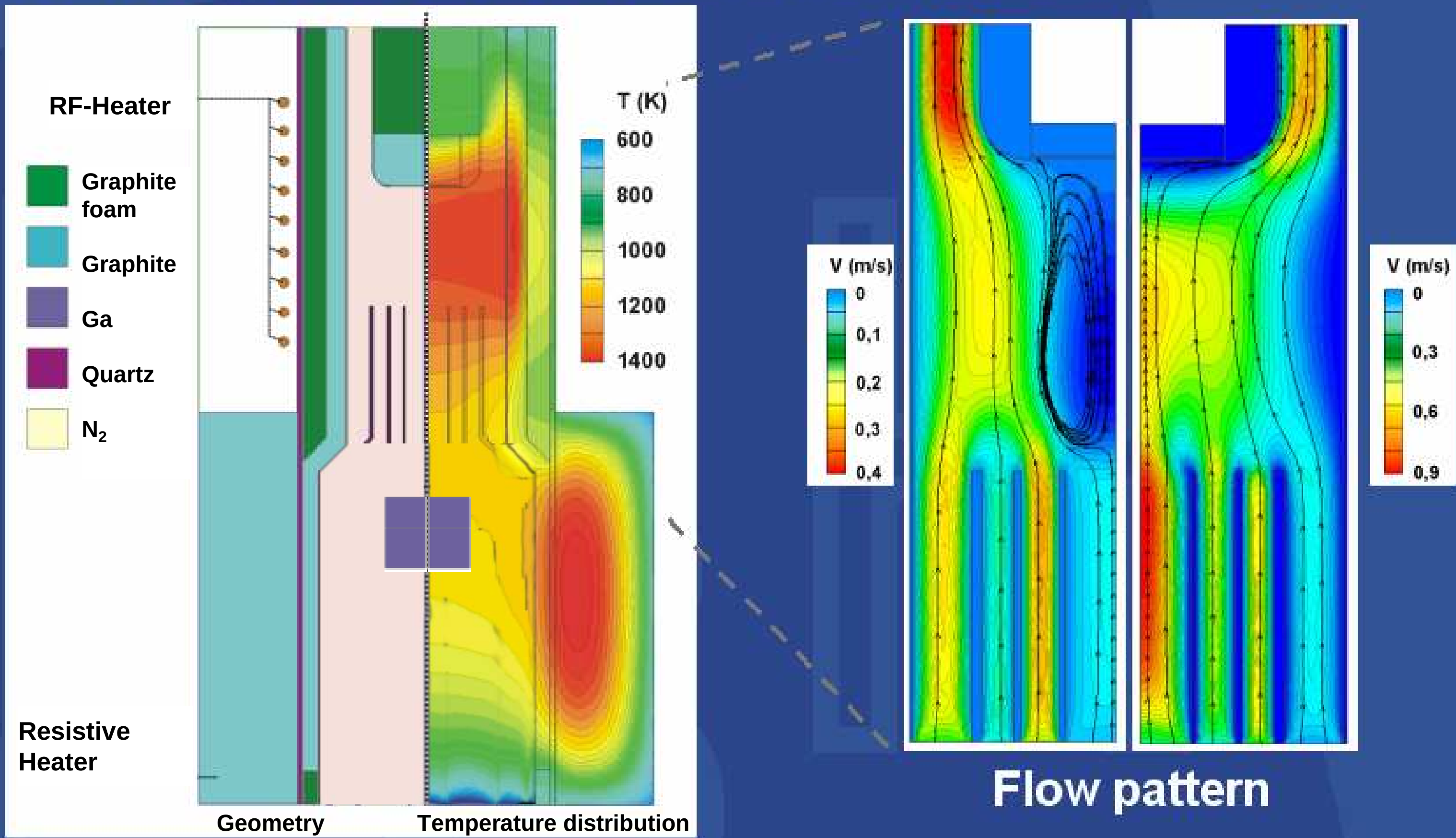
HEpiGaNS (STR)

- Heat Transfer
- Gas flow and species mass transport
- Quasi-thermodynamic model of heterogeneous chemical processes

- ➢ Temperature
- ➢ Flow pattern
- ➢ Species partial pressures
- ➢ GaN growth rate
- ➢ V/III ratio

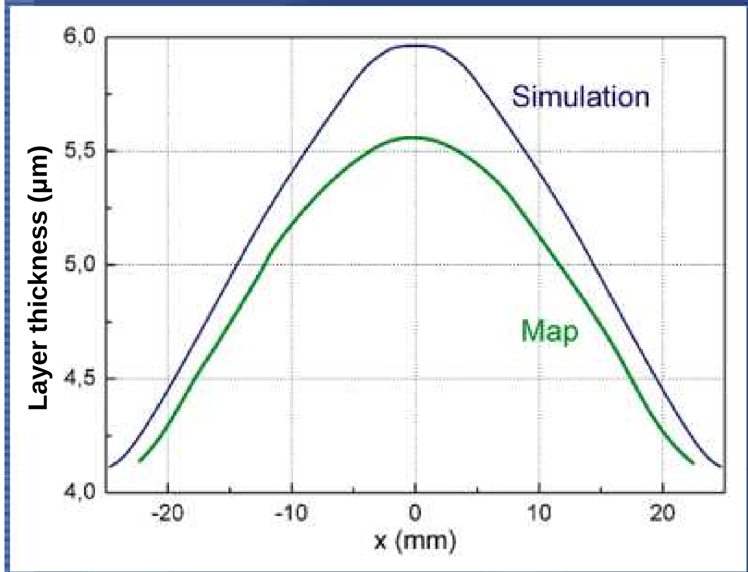
S. Hagedorn et al., DGKK Marburg 2007

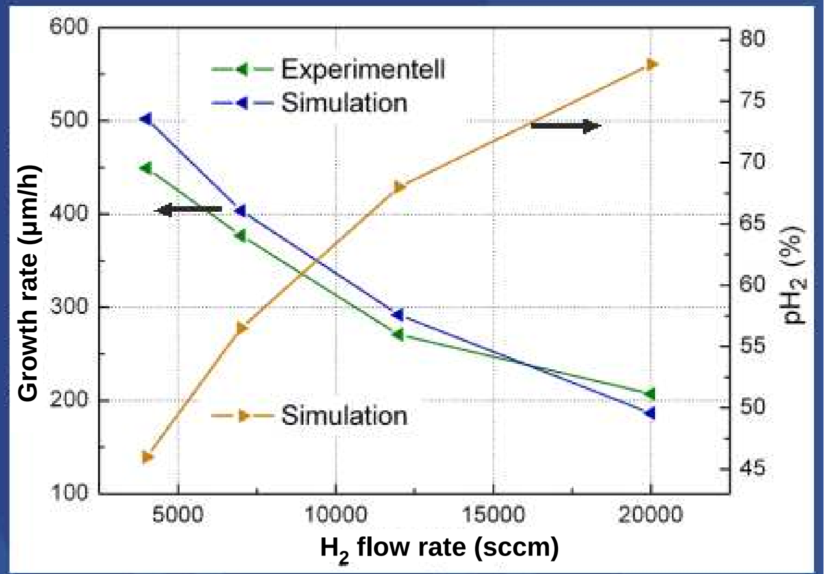
Temperature distribution and flow pattern



S. Hagedorn et al., DGKK Marburg 2007

Comparison of numerical predictions with experimental data





Effect of Hydrogen flow rate:
H_2 flow rate ↑ => GaN growth rate ↓

- **Good agreement between numerical and experimental data**
- **Simulation is necessary for growth control**

S. Hagedorn et al., DGKK Marburg 2007

Virtual Reactor is the effective tool for simulation of long-term growth of SiC/AlN/AlGaN crystals and epilayers

Any questions concerning software tools can be sent to **vr-support@str-soft.com**.

Publications, Physics Summary, GUI Manual, and presentations demonstrating editions of **Virtual Reactor** family, such as

- **VR-PVT SiC™**
- **VR-PVT AlN™**
- **HEpiGaNS™ (VR-HVPE GaN/AlGaN/AlN)**
- **VR-CVD SiC™**

are available upon request.