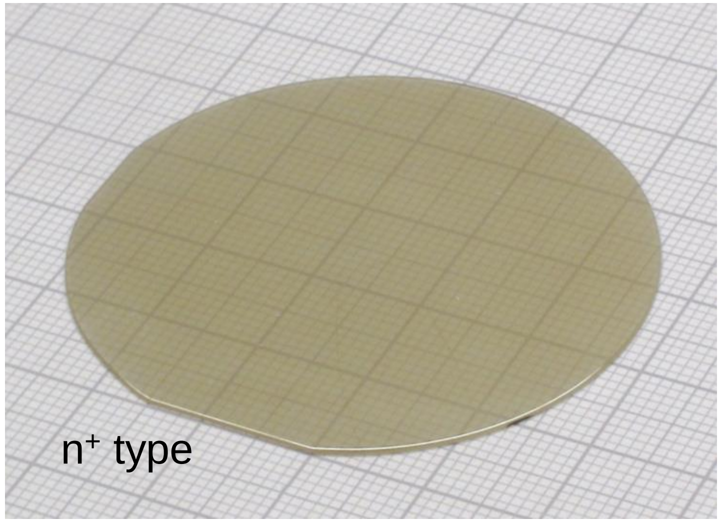
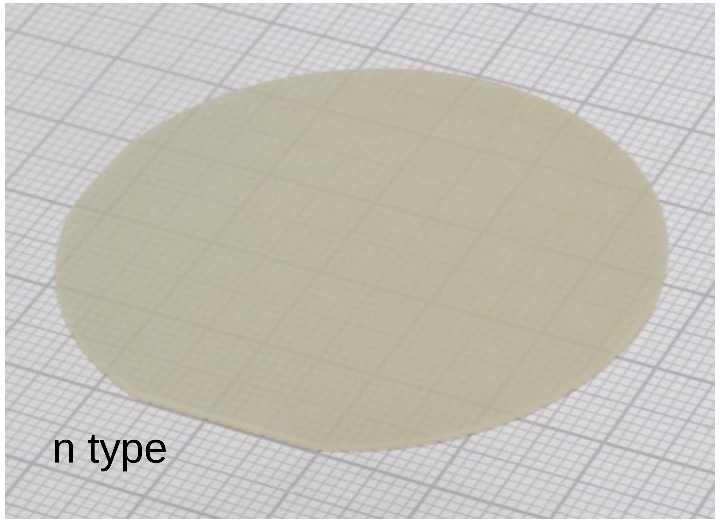
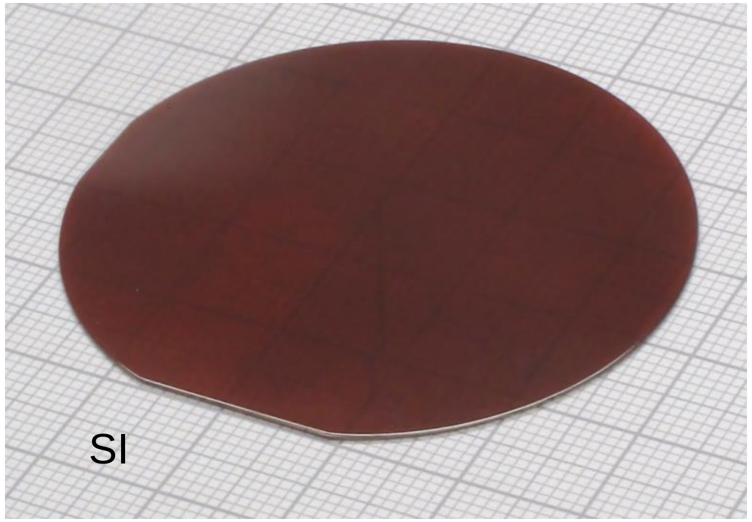
Towards GaN Substrates for Electronic and Optoelectronic Devices

Ammonothermal GaN Substrates





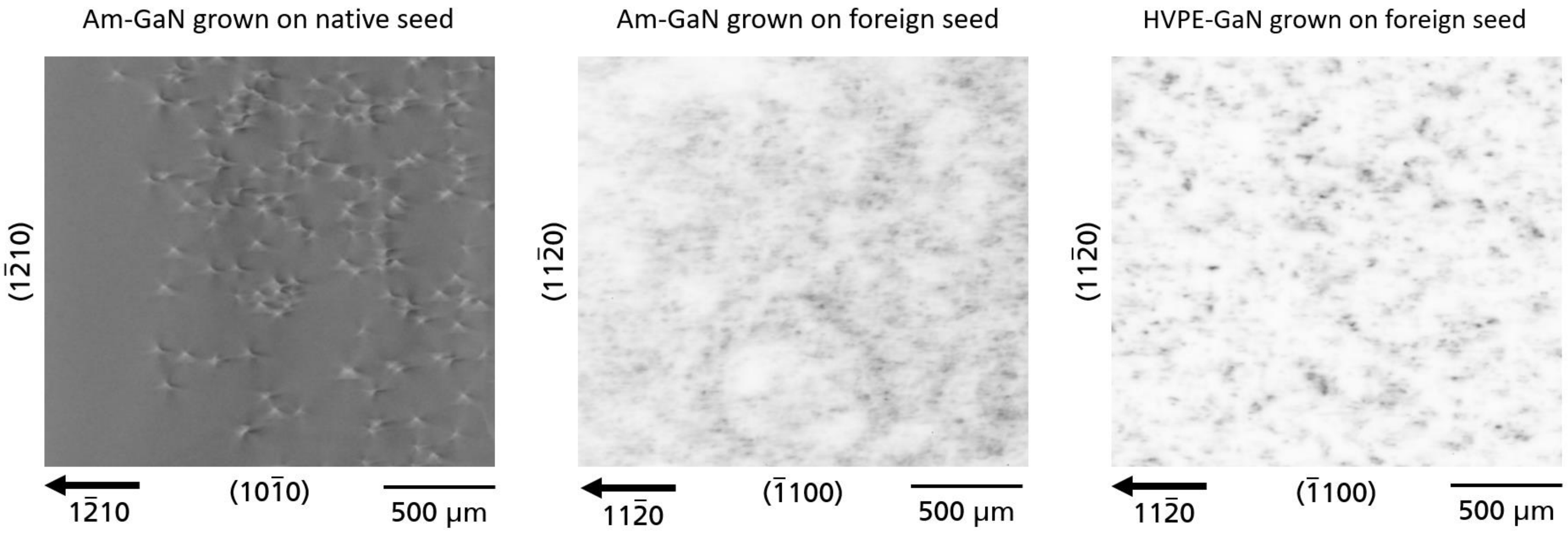


Material type	Conductivity type	Carrier concentration [cm^{-3}]	Carrier mobility [cm^2/Vs]	Resistivity [Ωcm]	Available size [inch]	Threading dislocation density [cm^{-2}]
High carrier concentration	n^+ type	~ 10^{19}	~150	10^{-3}	2	5×10^4
Low carrier concentration	n type	< 10^{18}	~250	10^{-2}	2	5×10^4
High resistivity (Mn-doped)	semi-insulating (SI)	-	-	≥10^8	2	5×10^4

Ammonothermal GaN Substrates – Structural Quality

- X-Ray Topography (XRT)

The Borrmann effect — dramatic increase in transparency for X-ray diffraction in transmission
robust method for evaluating the structural perfection of GaN
proof of the high perfection of the crystals

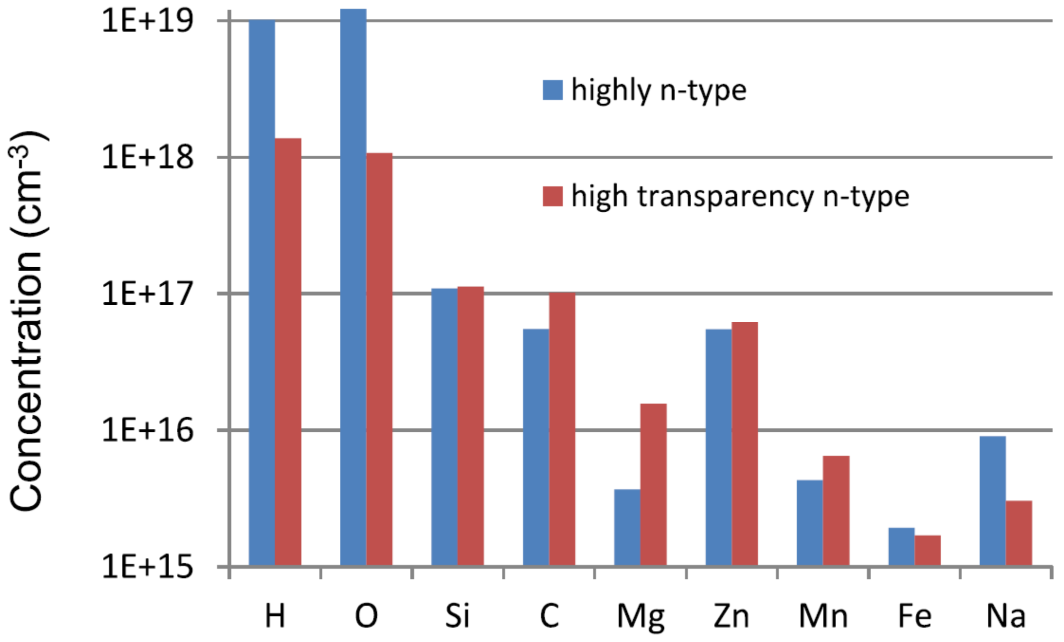


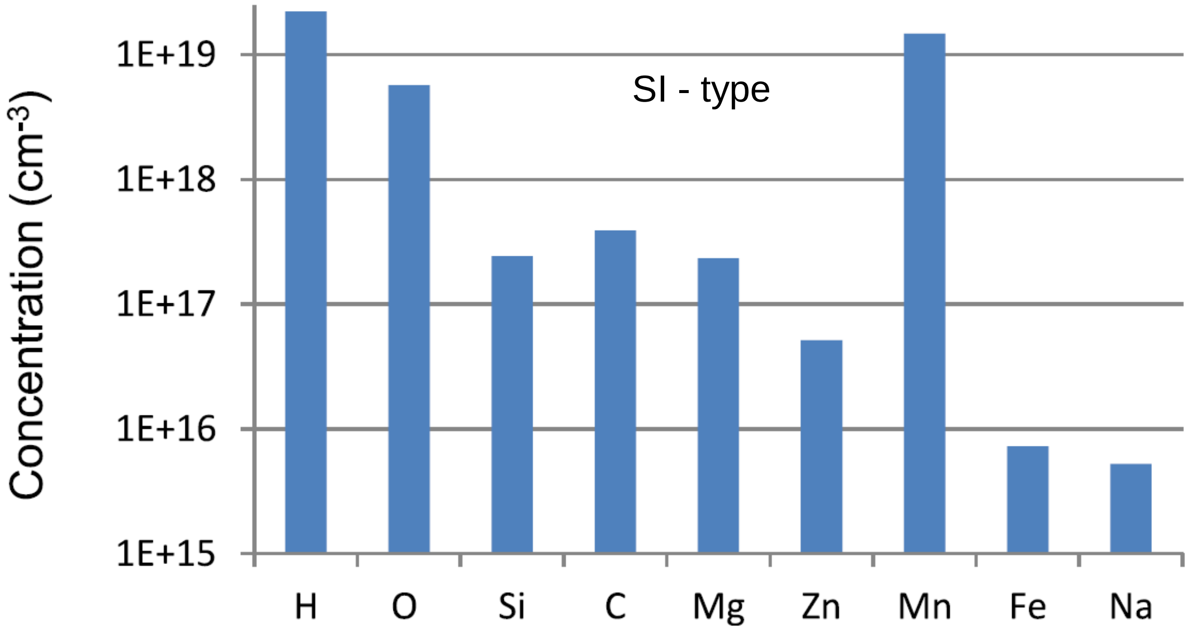
The Borrmann effect is blocked

L. Kirste et al., Materials 2021, 14, 5472.

Ammonothermal GaN Substrates – Point Defects

- Secondary Ion Mass Spectrometry



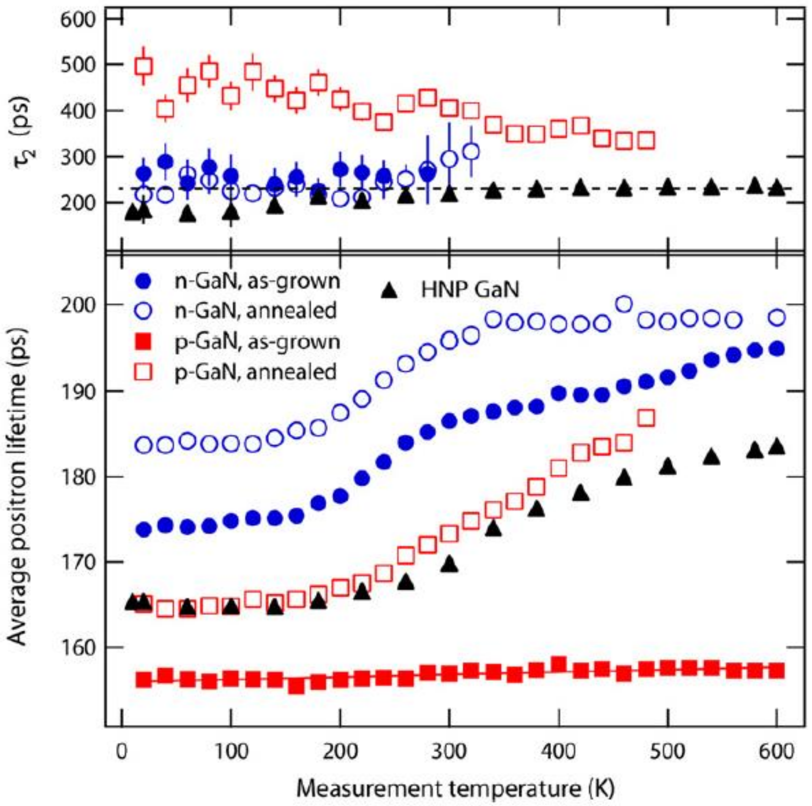


M. Zajac et al., Progress in Crystal Growth and Characterization of Materials 64 (2018) 63–74.

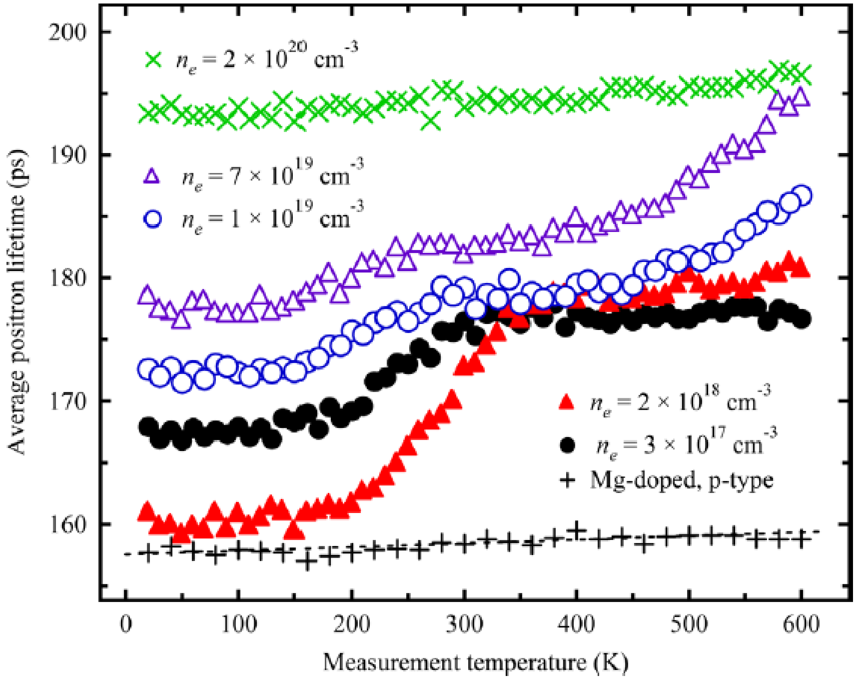
Ammonothermal GaN Substrates – Point Defects

- Positron Annihilation Spectroscopy

$V_{Ga} = \sim 10^{19}\ cm^{-3}$



- the positron lifetimes suggest that V_{Ga} are complexed with hydrogen impurities
- vacancy-hydrogen complexes play an important role as autocompensating centers in oxygen-doped Ammono-GaN

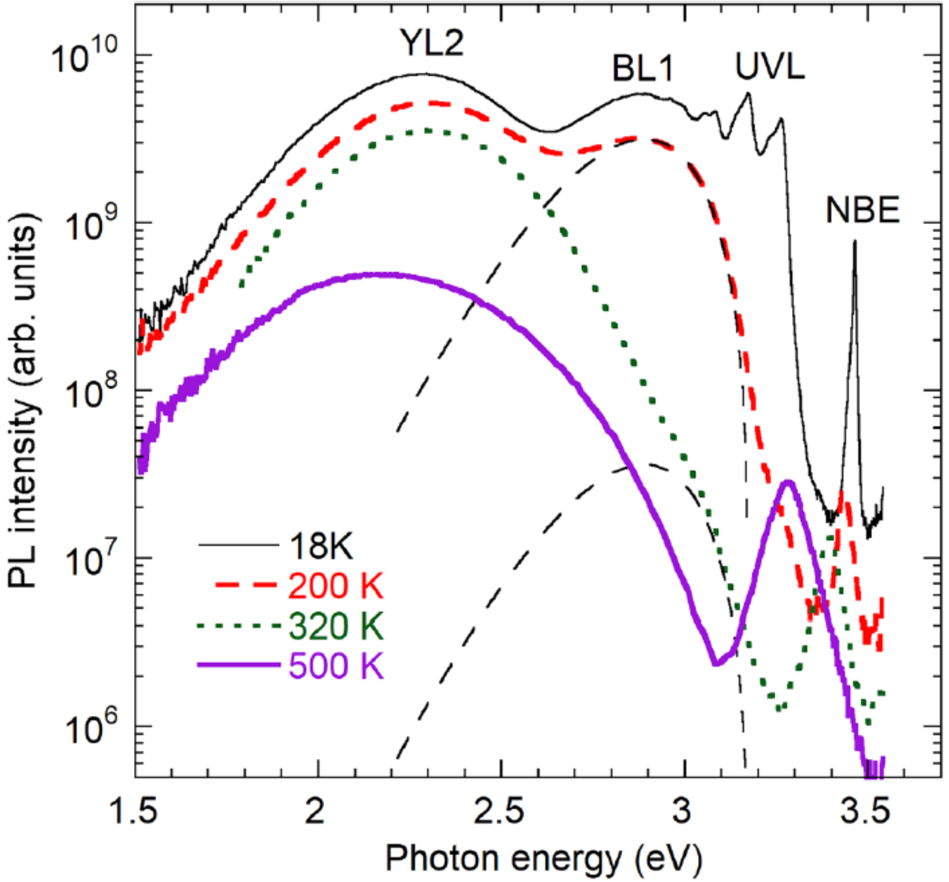


F. Tuomisto et al., Journal of Crystal Growth 312 (2010) 2620-2623

F. Tuomisto et al., Journal of Crystal Growth 403 (2014) 114-118

Ammonothermal GaN Substrates – Point Defects

- Photoluminescence

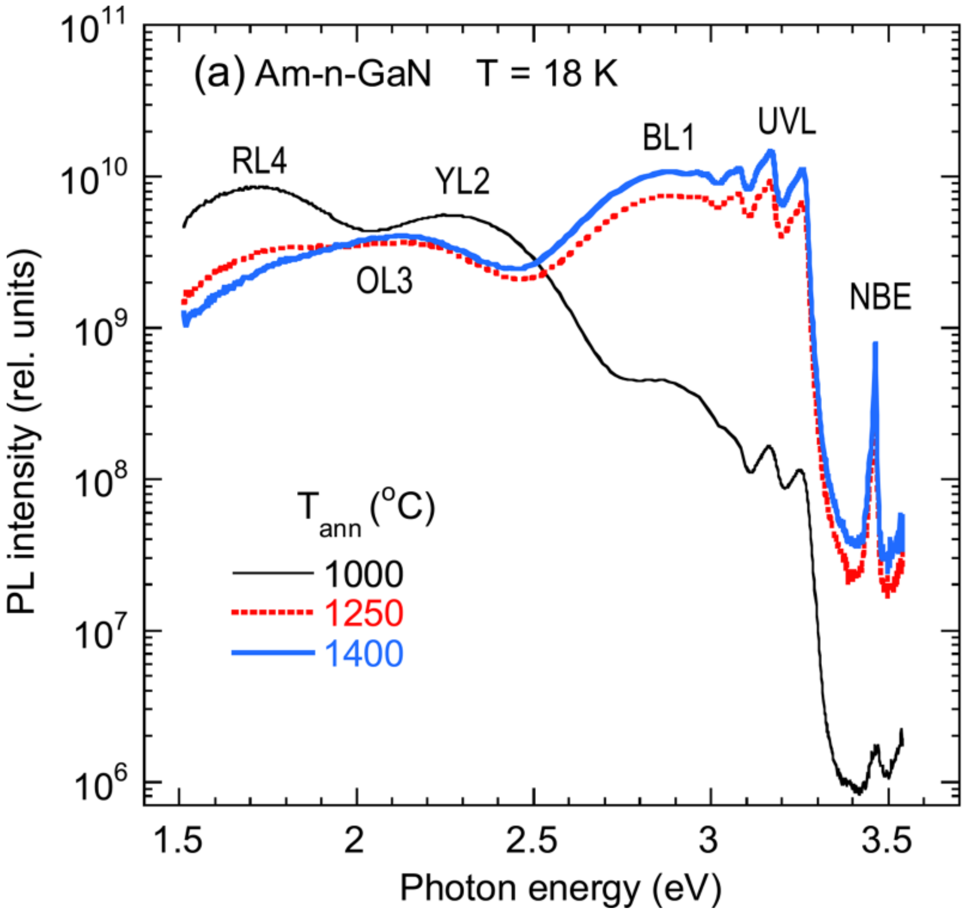


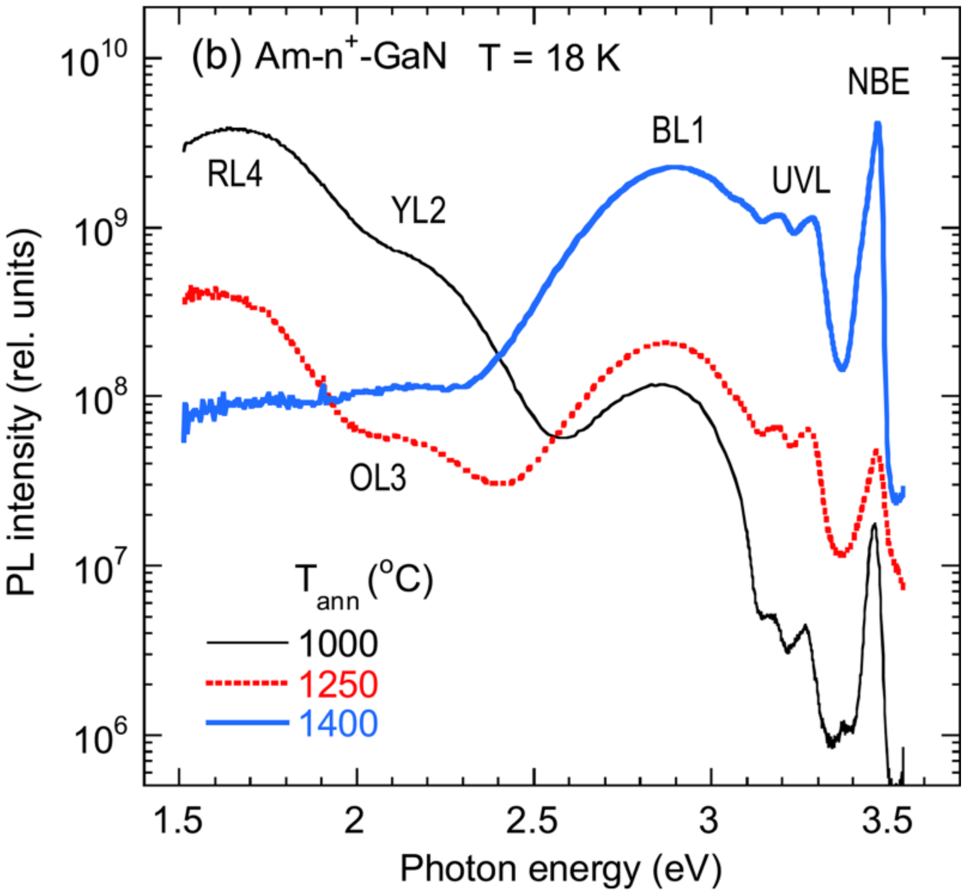
PL band	Preliminary attribution	(eV)
UVL	Mg_{Ga}	3.27
BL1	Zn_{Ga}	2.86
YL2	V_{Ga}-$3H_i$	2.3
OL3	Unknown	2.09
RL4 in n-type	V_{Ga}-$3O_N$	1.7
RL4 in n^+-type	V_{Ga}-$3O_N$	1.6

M.A. Reshchikov et al., J. Appl. Phys. 129, 095703 (2021)

Ammonothermal GaN Substrates – Point Defects

- Photoluminescence

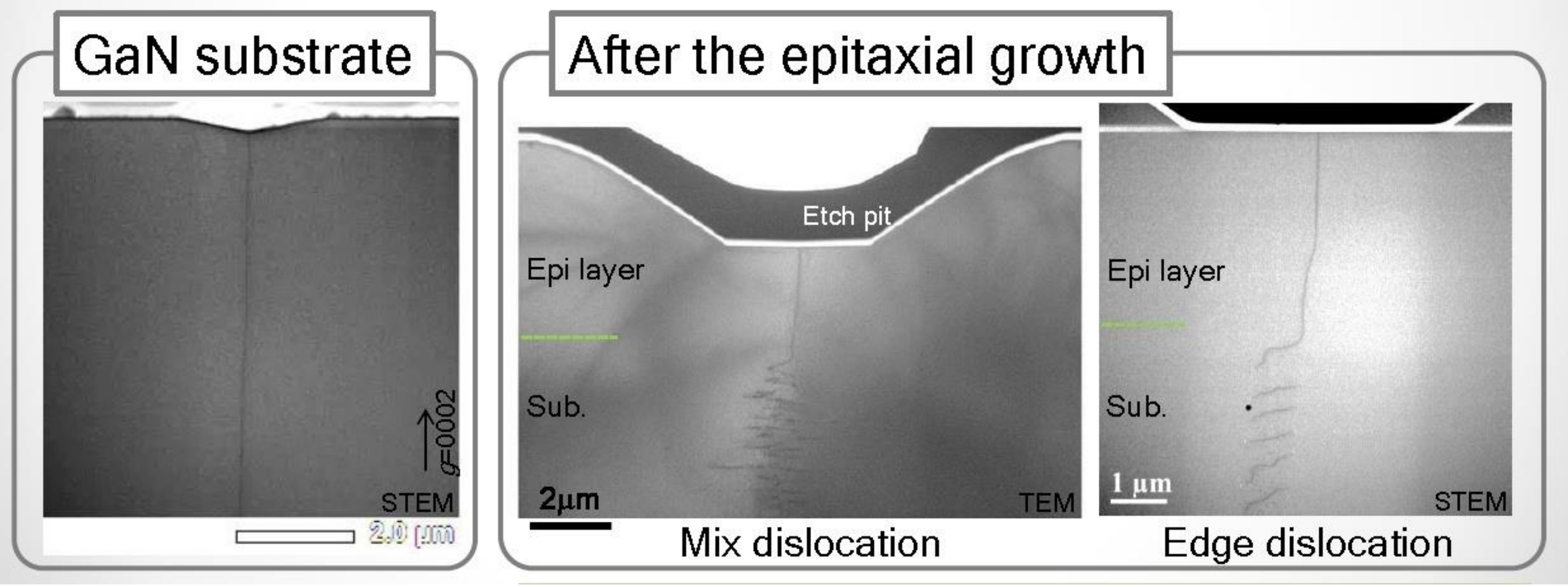




M.A. Reshchikov et al., J. Appl. Phys. 131, 035704 (2022)

Ammonothermal GaN Substrates – Point Defects

- Star-like Defects

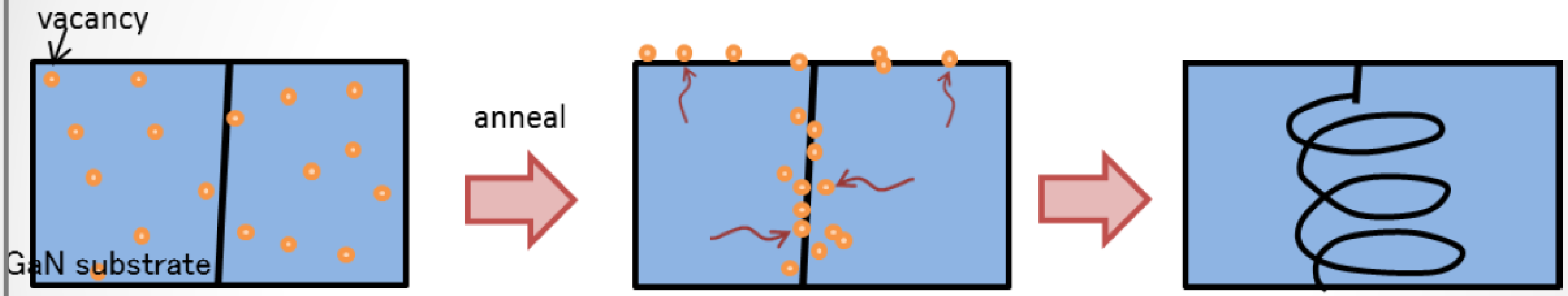


K. Horibuchi et. al, Semicond. Sci. Technol. 31 (2016) 034002.

Ammonothermal GaN Substrates – Point Defects

Deformation mechanism of Helical dislocation

Formed by an interaction between the dislocation and the vacancies

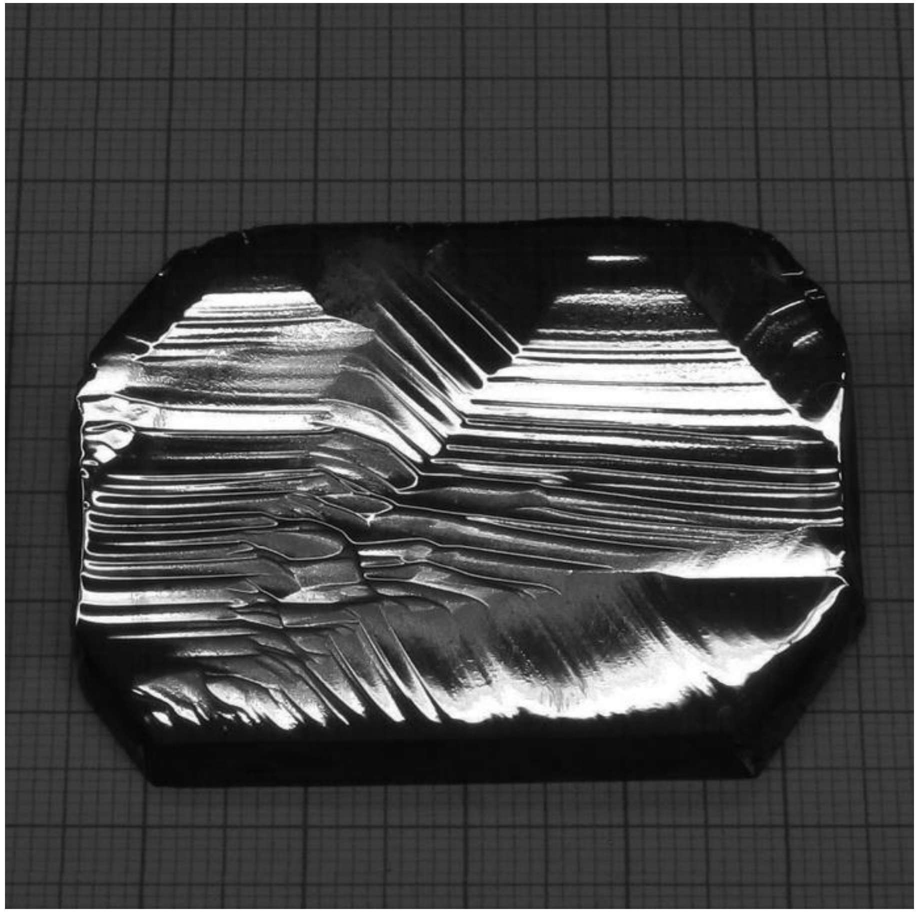


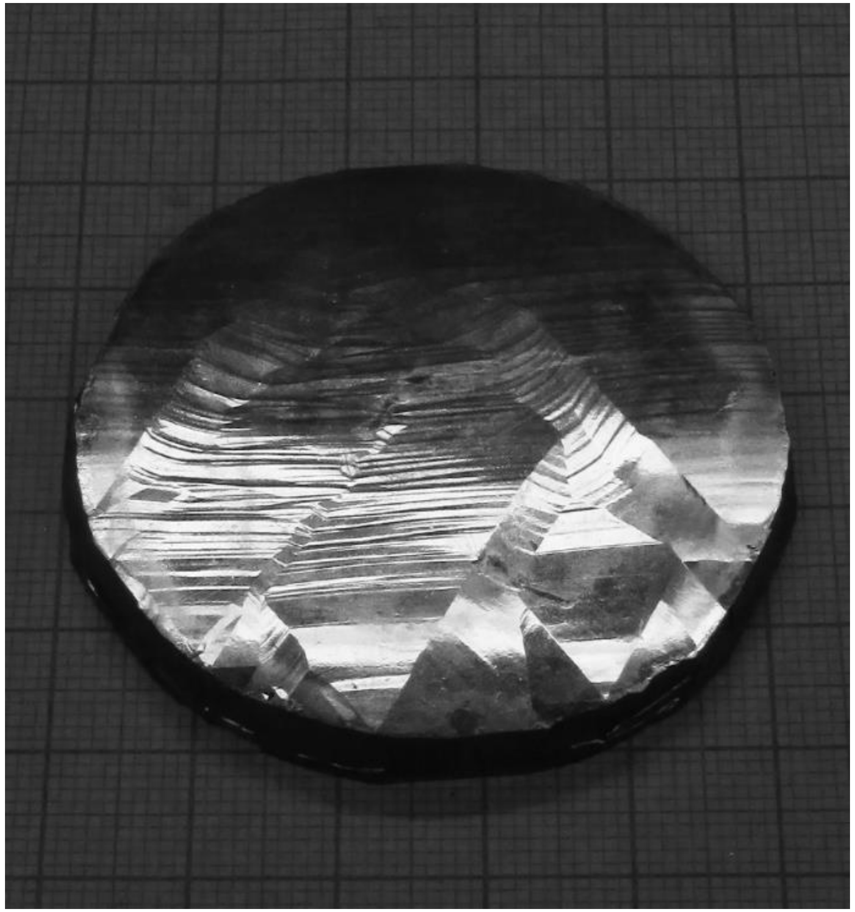
Observed after a heat treatment of a low-dislocation single crystal (Al, Cu, Si and GaAs)

<u>First observation in the GaN crystal</u>

K. Horibuchi et. al, Semicond. Sci. Technol. 31 (2016) 034002.

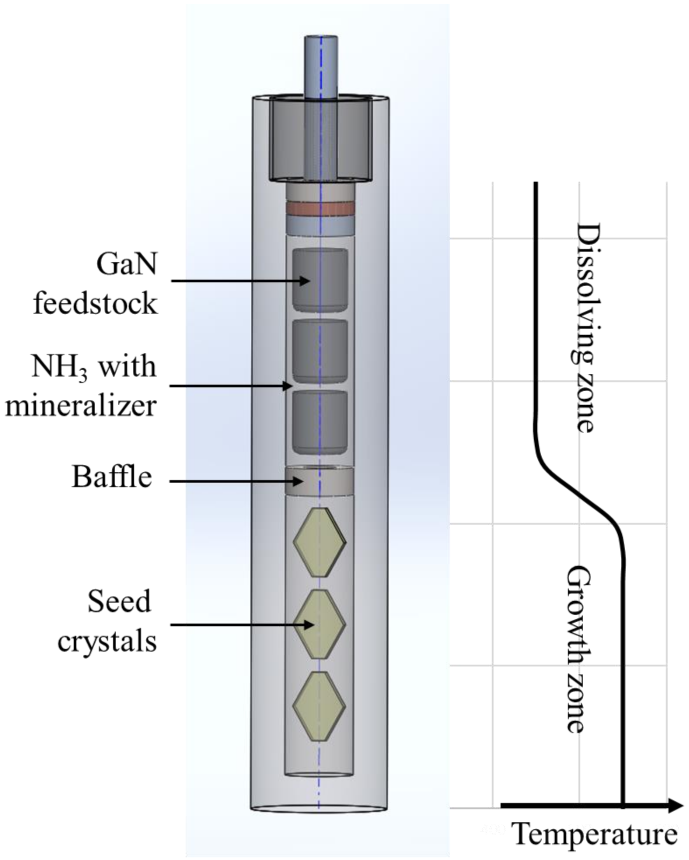
Ammonothermal GaN Crystals



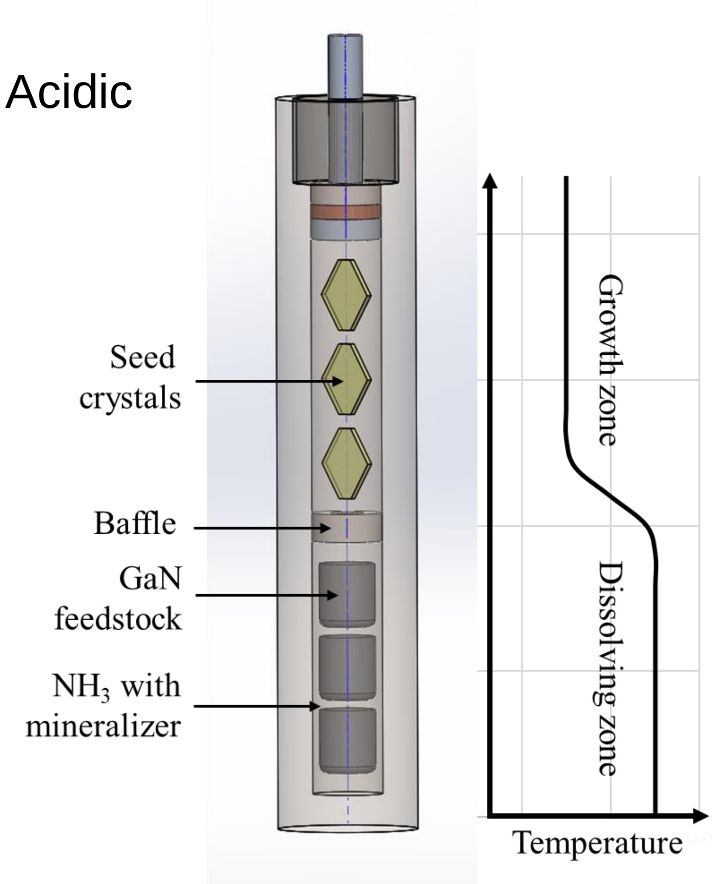


Ammonothermal Growth Methods

- Basic



- Acidic



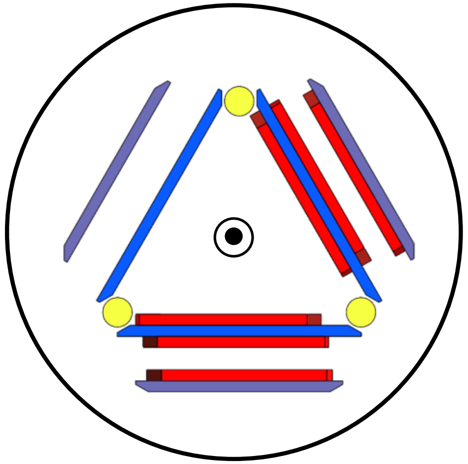
- Mineralizers: Alkali metals Halide compounds

Ammonothermal Growth Method

Seed selection

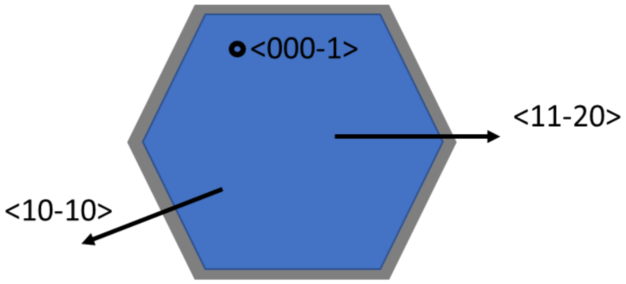
Mounting
on metal plate

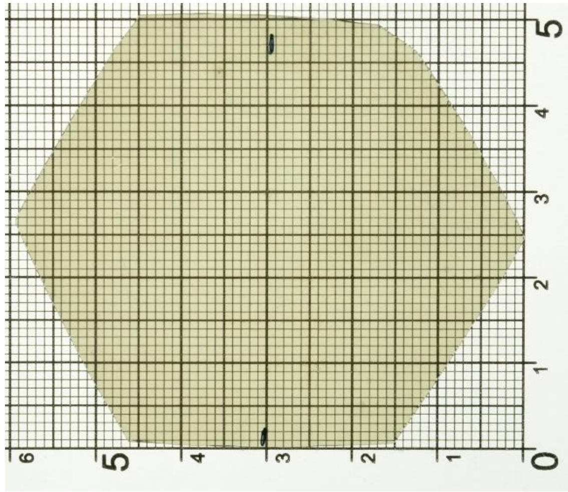
Growth zone

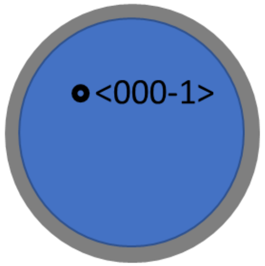


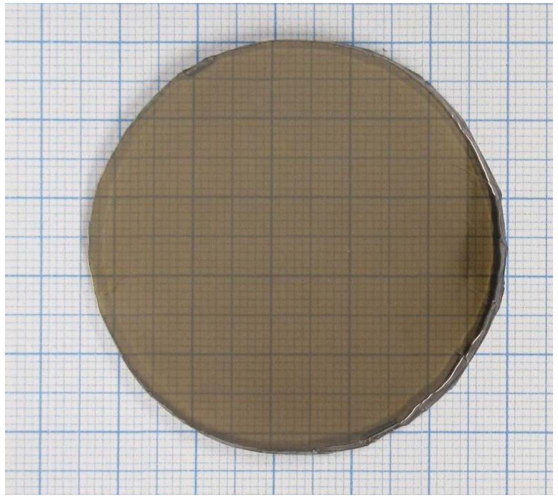
Ammonothermal Growth Method

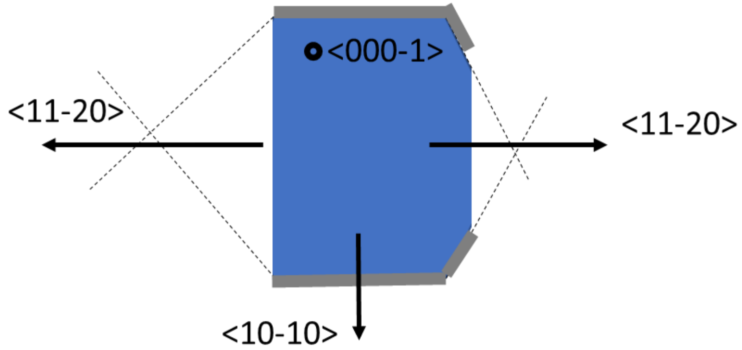
Blocking growth in lateral direction by metal borders

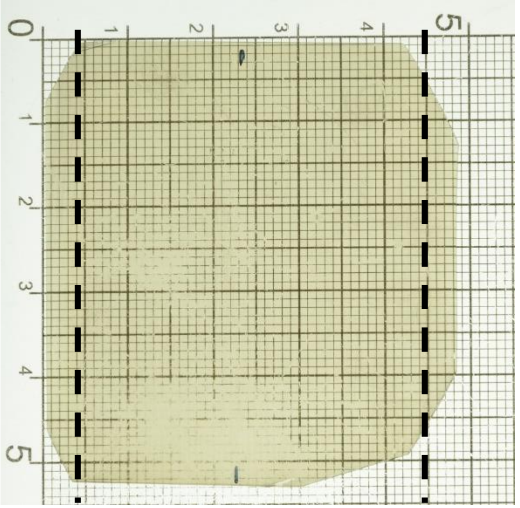


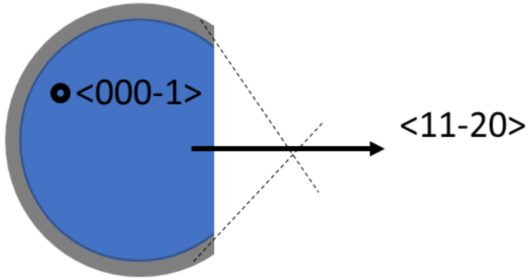


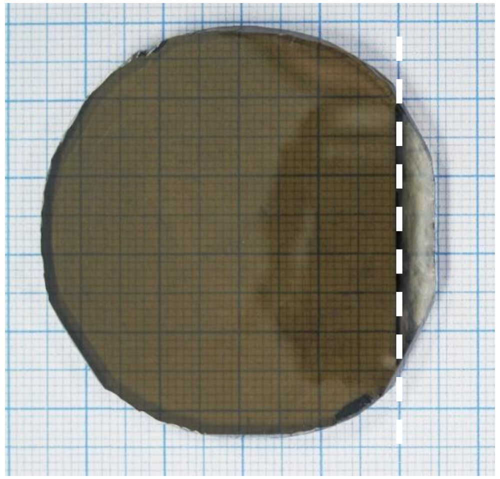






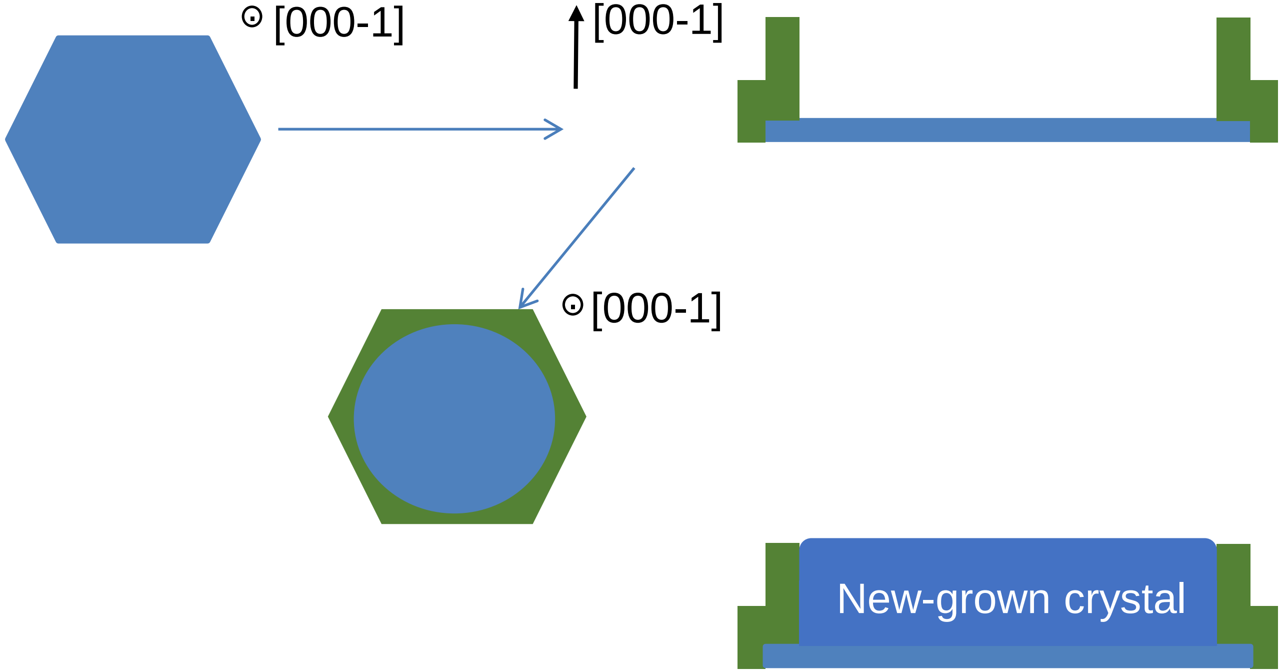


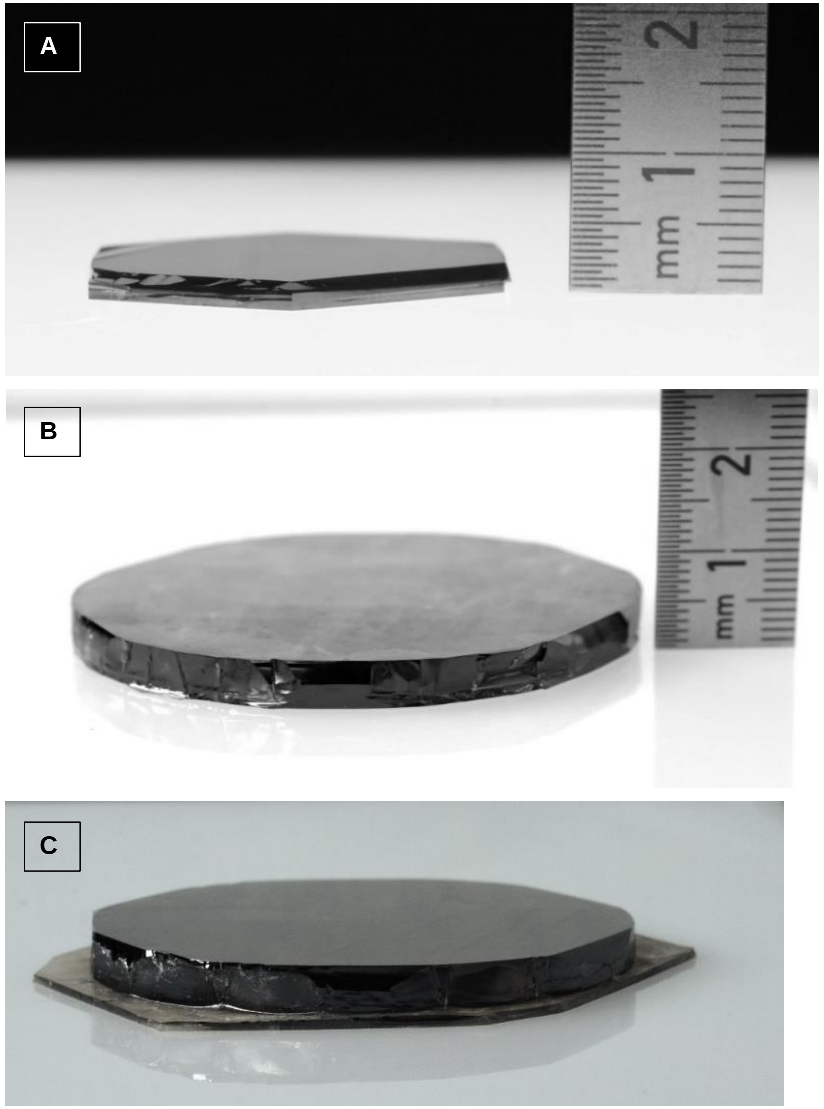




K. Grabianska et al., J. Cryst. Growth 547 (2020) 125804

Ammonothermal Growth Method

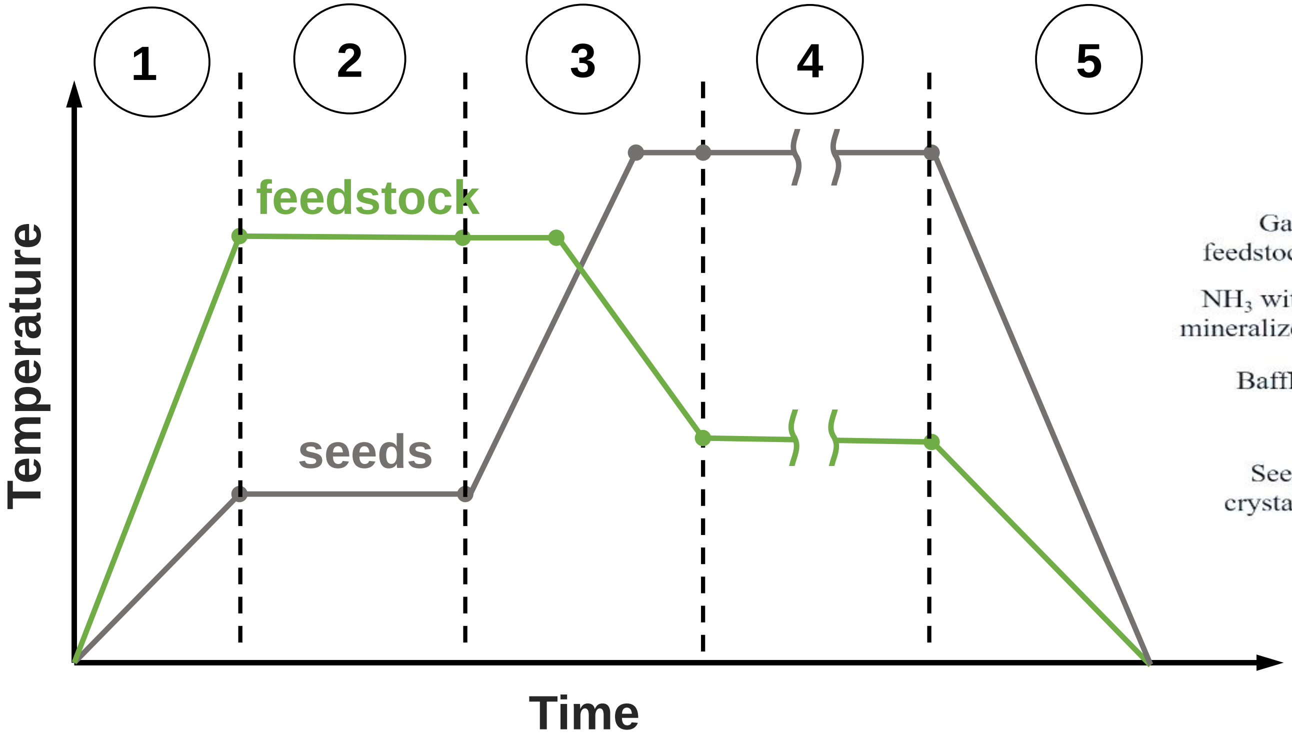


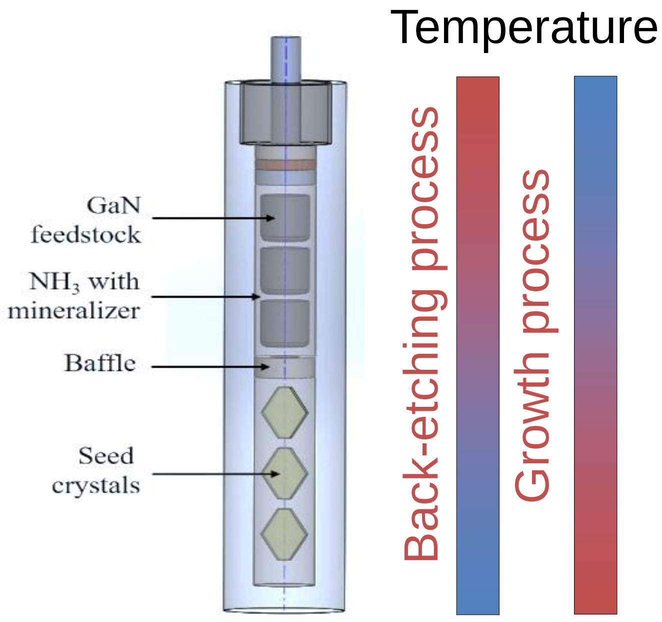


R. Kucharski, K. Grabianska

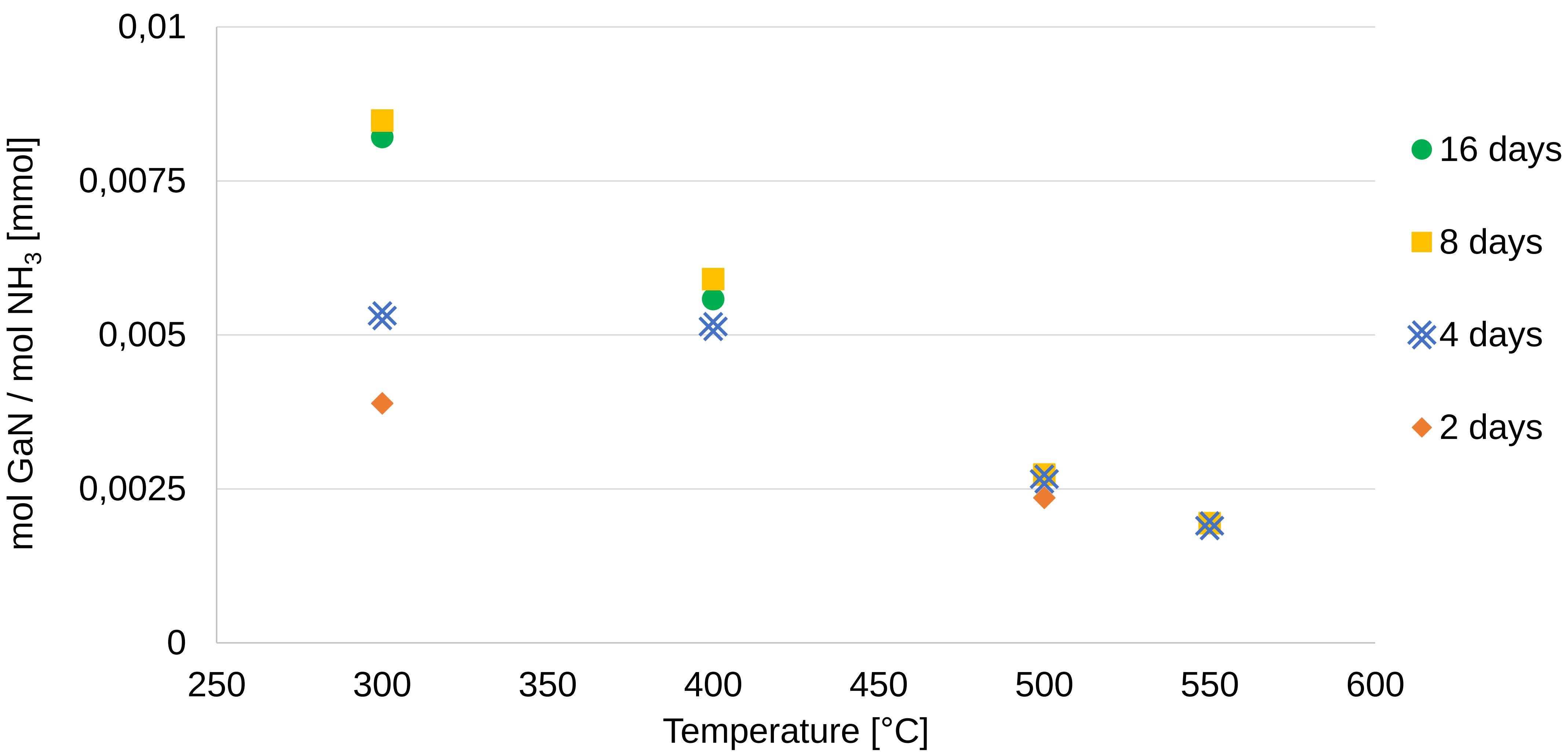
Ammonothermal Growth Method – Stages

1. Heat-up
2. Back-etching of the seeds at lower temperature
3. Temperature transition
4. Growth at higher temperature/dissolution of the feedstock at lower temperature
5. Cool-down





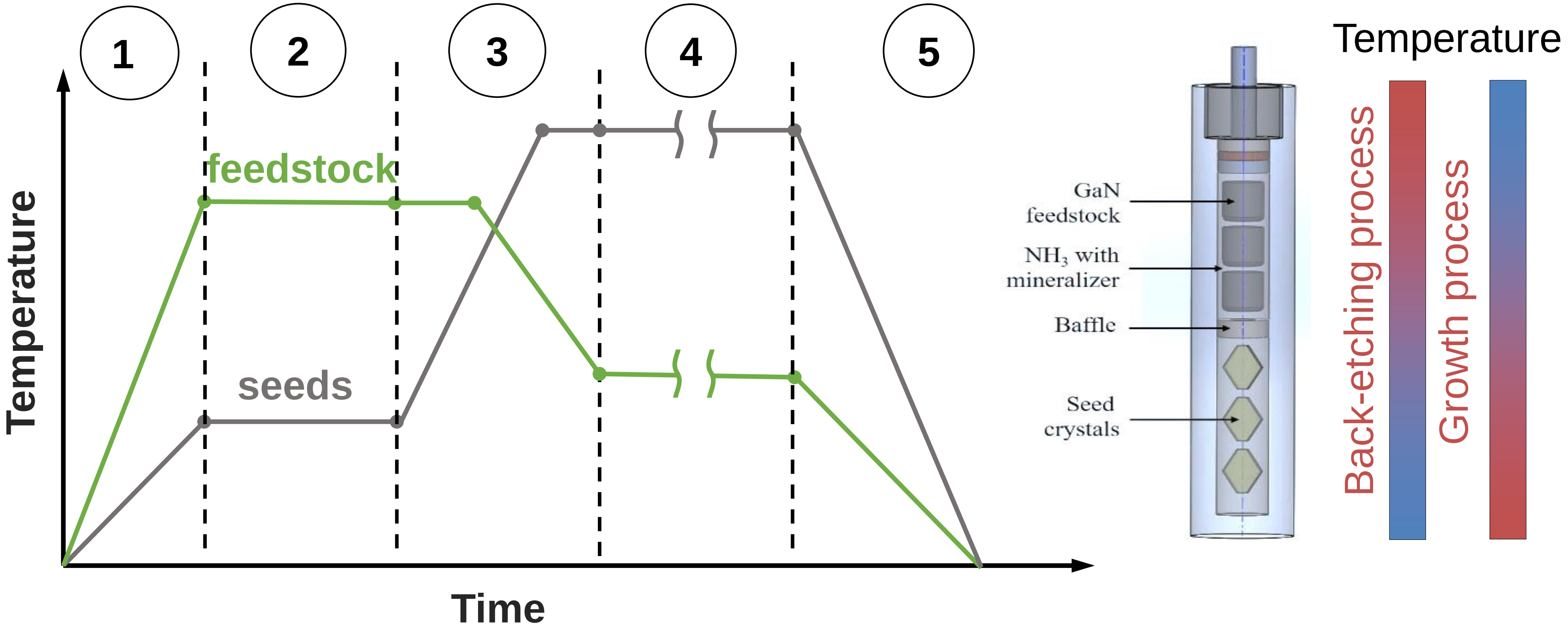
Retrograde Solubility Mode



R. Kucharski, K. Grabianska

Ammonothermal Growth Method – Stages

1. Heat-up
2. Back-etching of the seeds at lower temperature
3. Temperature transition
4. Growth at higher temperature/dissolution of the feedstock at lower temperature
5. Cool-down

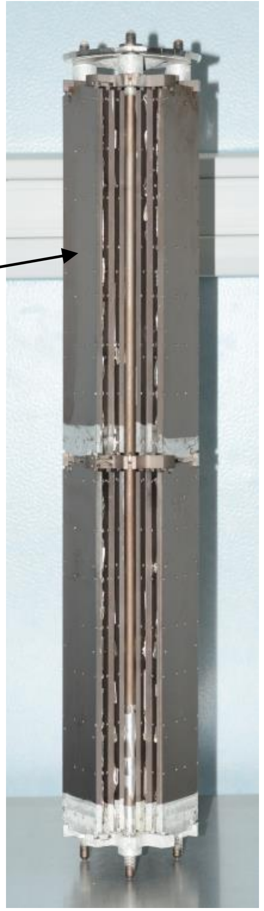


Ammonothermal GaN Crystals

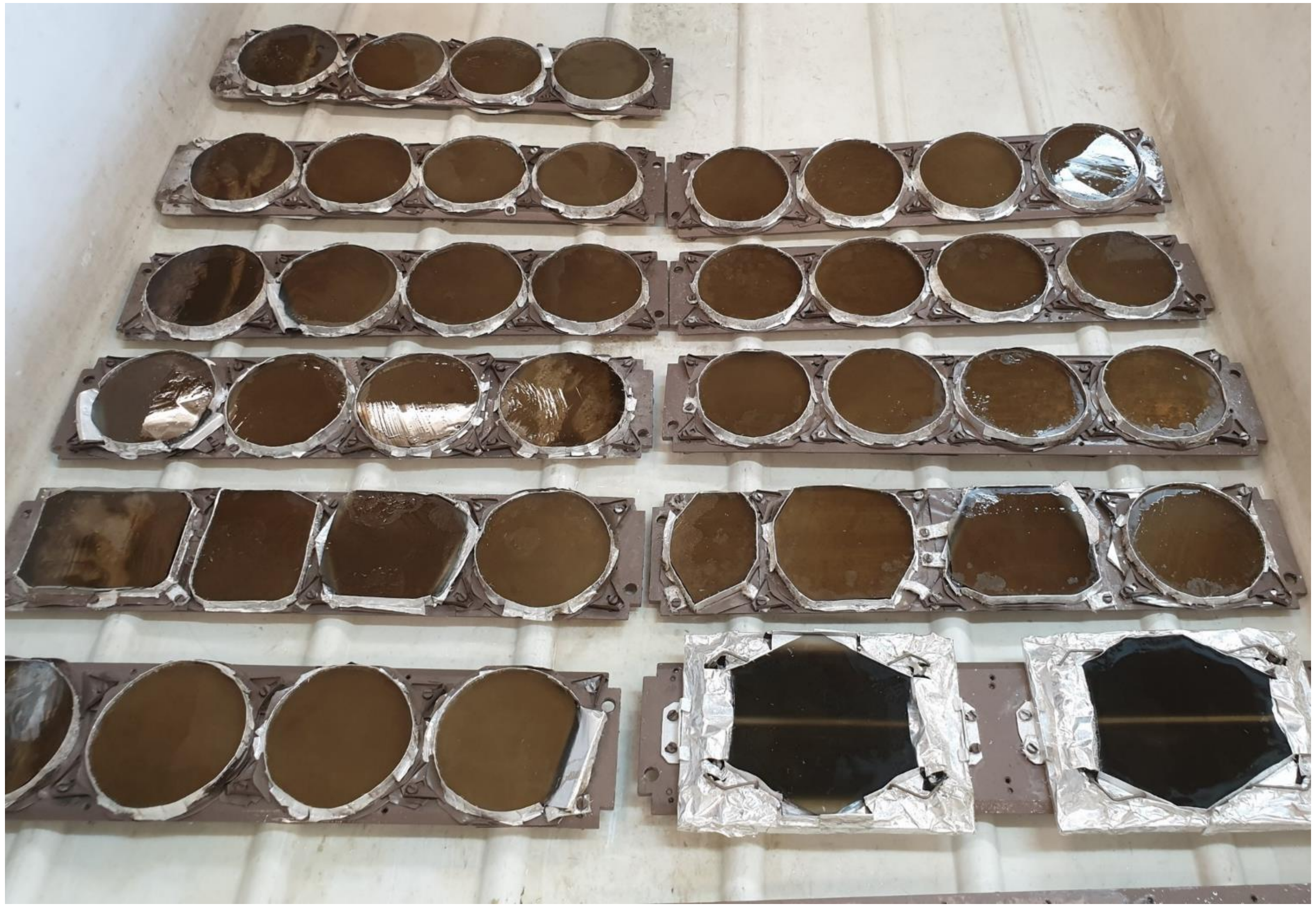
Seed selection

Mounting
on metal plate

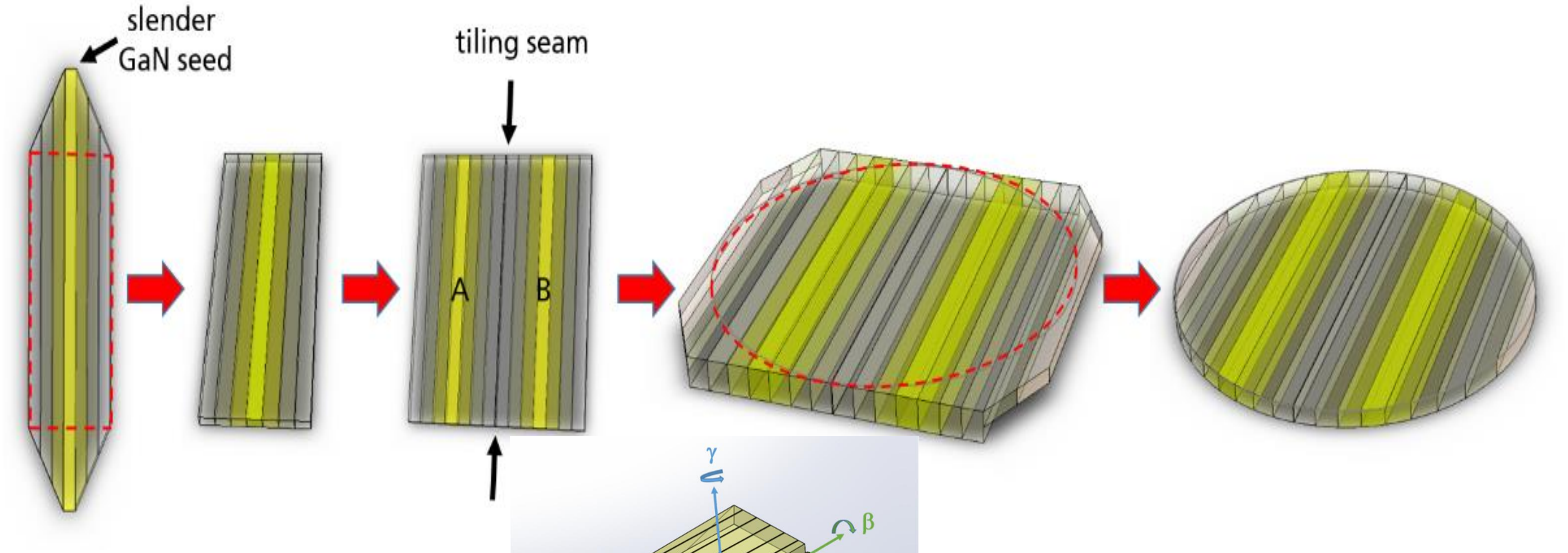
Growth zone

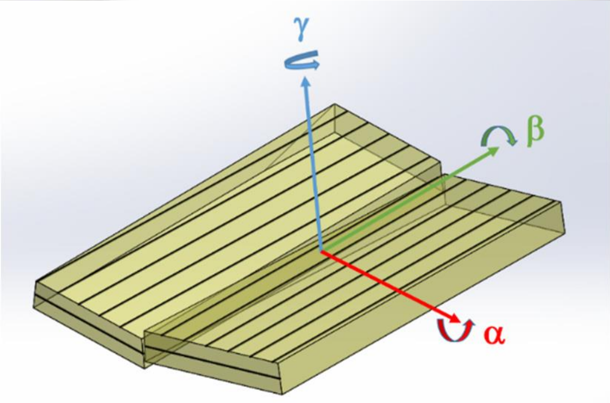


After growth process



Ammonothermal Growth Method – Tiling





The angular differences of α, β and γ are smaller than the variation of crystal off-cut.

L. Kirste et al., Materials 2021, 14, 5472.

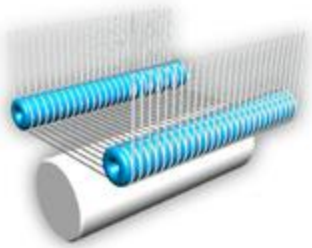
Wafering Procedures – The Way to Obtain Substrates

Pulling Single Crystal Silicon Ingots

Single Crystal Silicon Ingots

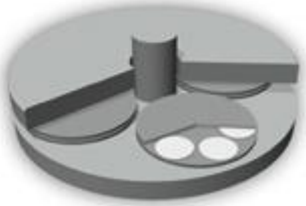
Peripheral Grinding

An ingot with a notch

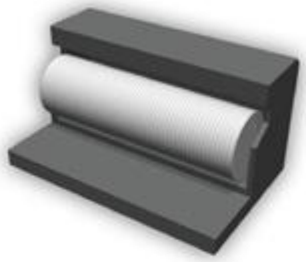


Slicing

Beveling (Peripheral Rounding)



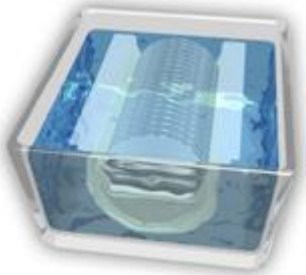
Lapping (Double Side Lapping)



Etching (Chemical Polishing)

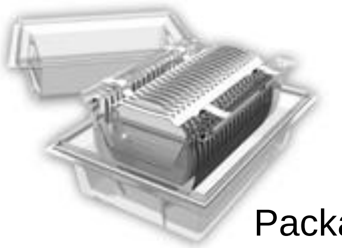
Heat Treatment to Remove Unstable Donors

Polishing (Single Side Mirror Polishing)



Cleaning

Inspections

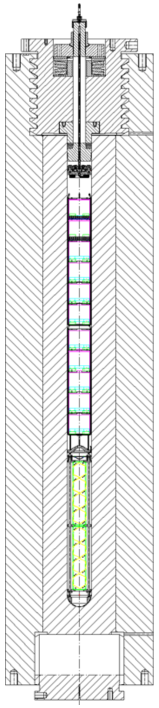


Packaging

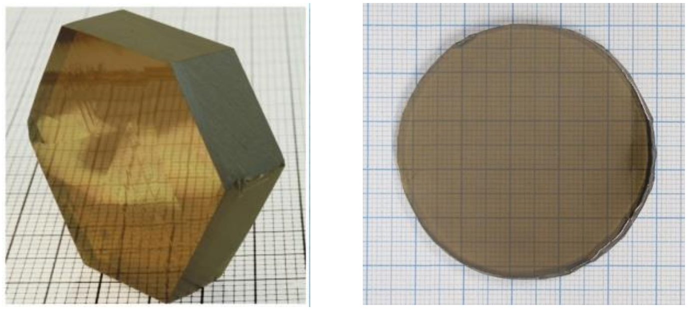
Shipping

Silicon Wafer Production Process | GlobalWafers Japan (sas-globalwafers.co.jp)

Production of Ammonothermal GaN Substrates



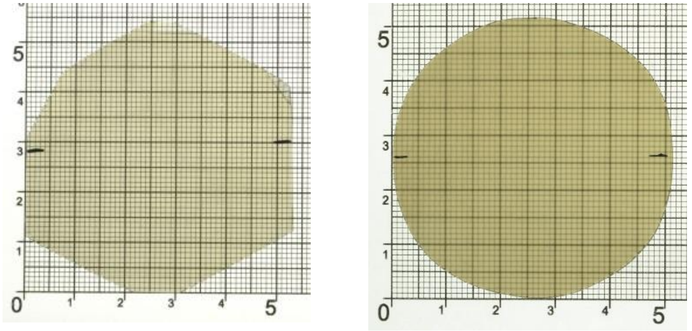
Crystallization



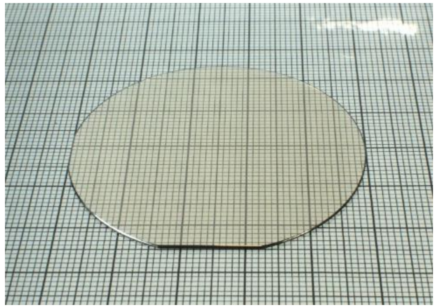
As-grown crystals

Machining process

Seeds



Substrate



Wafering Procedures

1. The new-grown crystal is sliced off from its seed (a wire saw is used)
2. The (10-10) facet is found (a measuring device (gauge) and a goniometer are used)

a)

b)

3. The (0001) facet is found (a goniometer and a CNC machine are used)

Goniometer:
an instrument for the precise measurement of angles, especially one used to measure the angles between the faces of crystals.

CNC

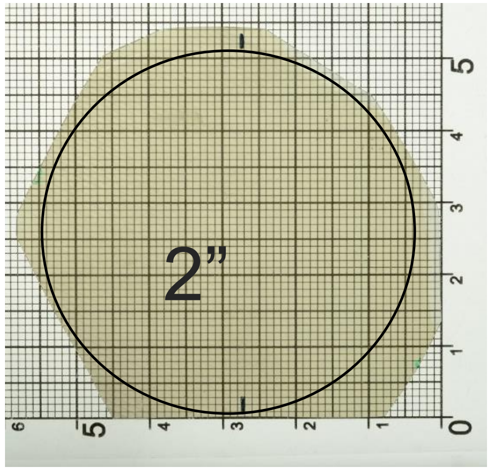
R. Kucharski, J. Skladanowski

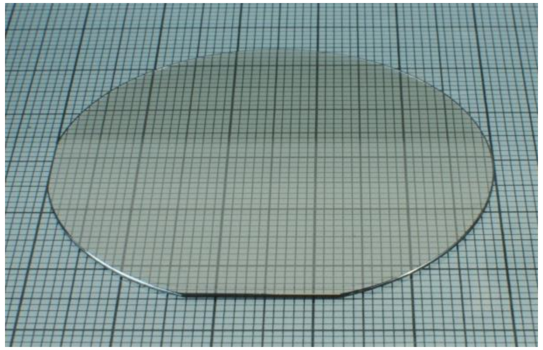
Wafering Procedures

Wafering Procedures

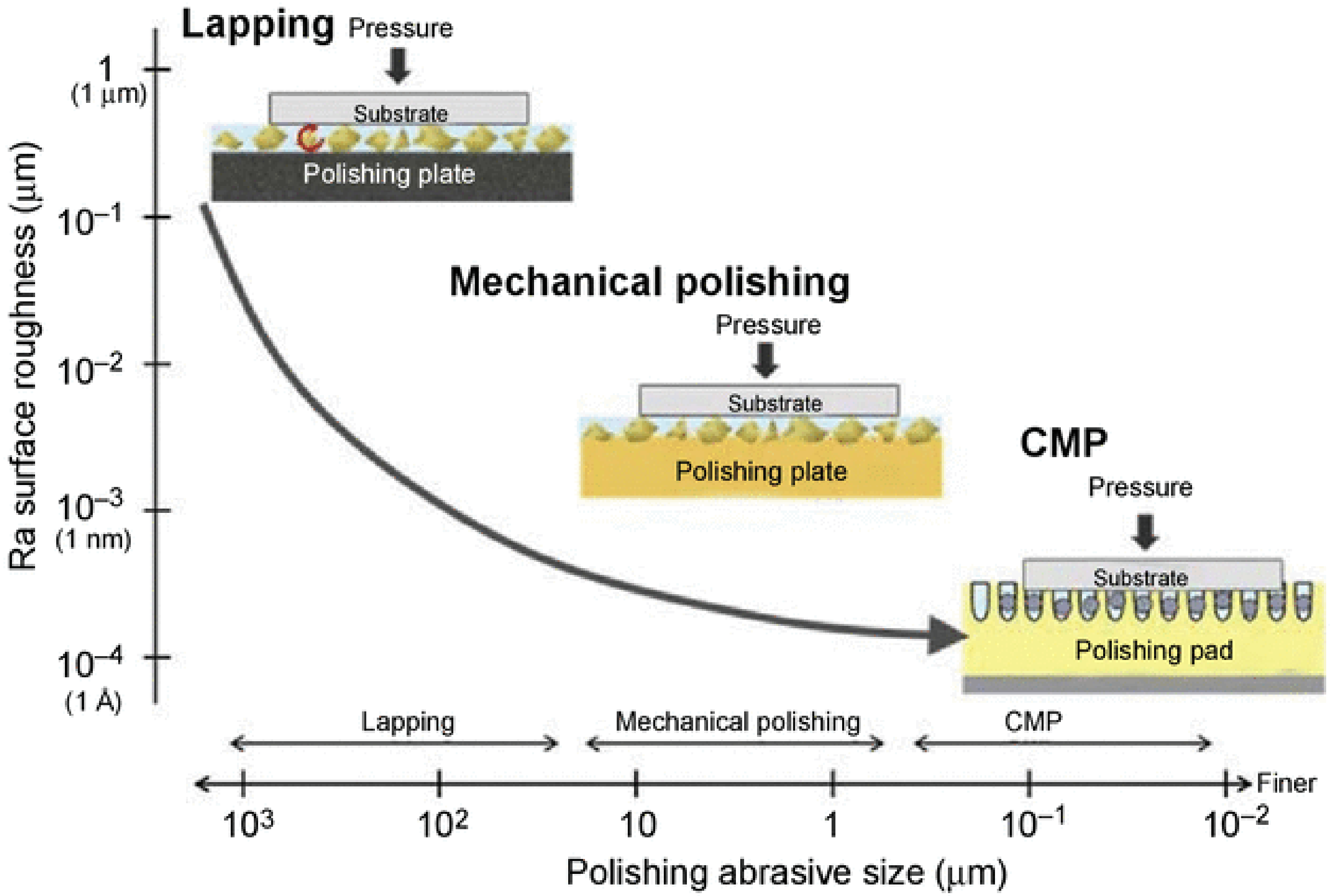
General specification

DESCRIPTION		UNIT	VALUE
	Orientation		(0001) C plane
	Thickness	µm	500 (±50)
	Dimension(s)	mm	Ø50,4 (±0,6)
	Primary Flat (PF)	mm	16 (±1)
	Secondary Flat (SF)	mm	8 (±1)
	Bow	µm	0 (±20)
	Total Thickness Variation (TTV)	µm	≤ 60





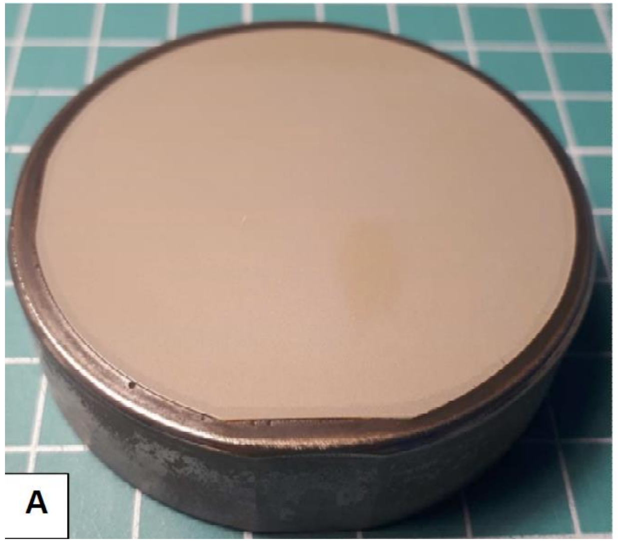
Wafering Procedures

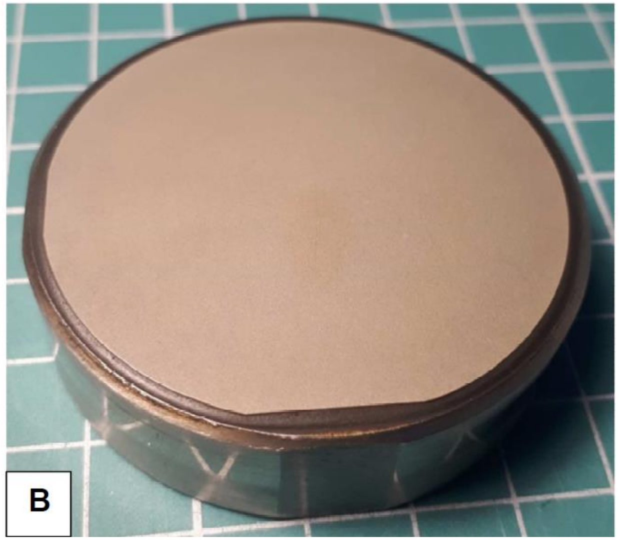


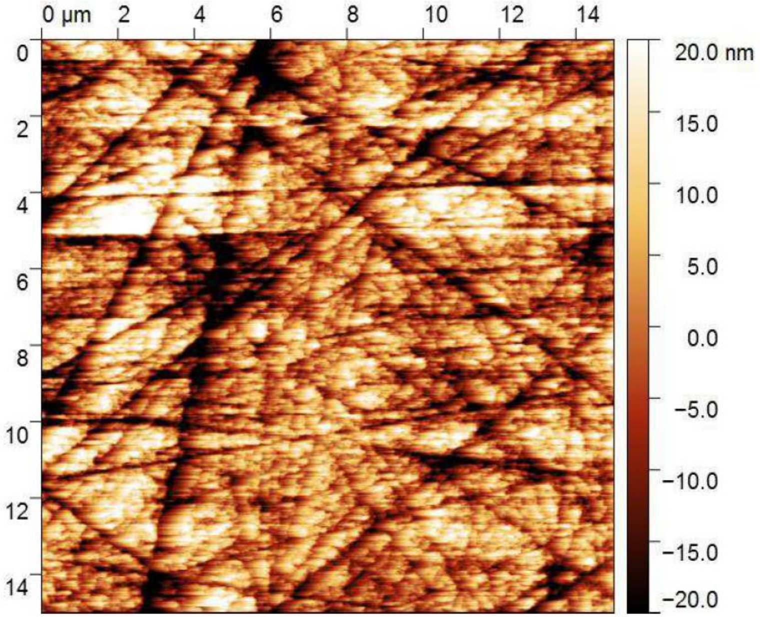
Steps:

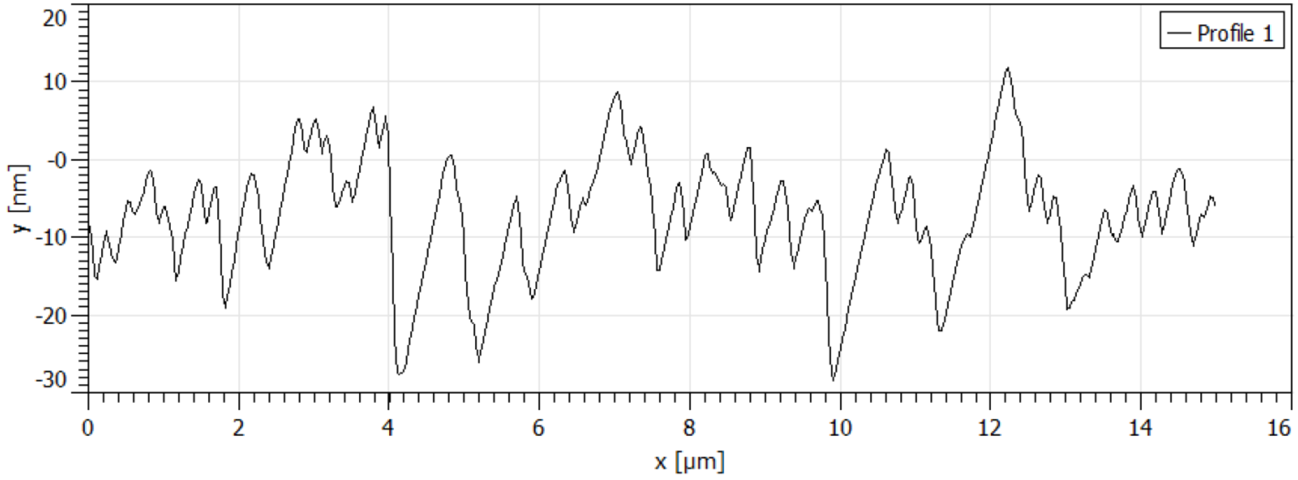
1. Surface and edge grinding
2. Lapping
3. Mechanical polishing
4. Chemo-mechanical polishing

Wafering Procedures



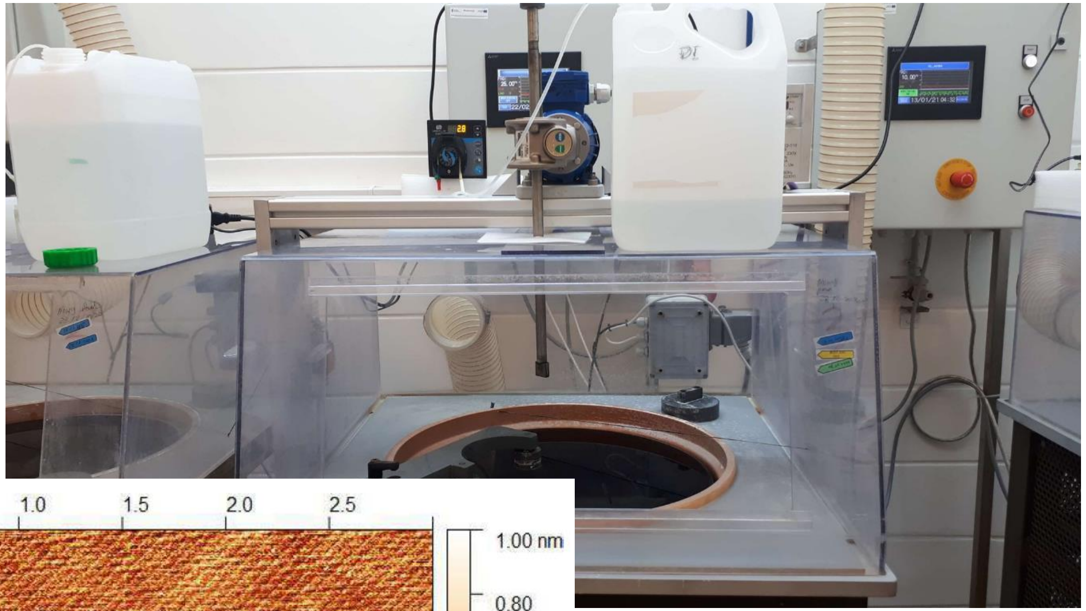


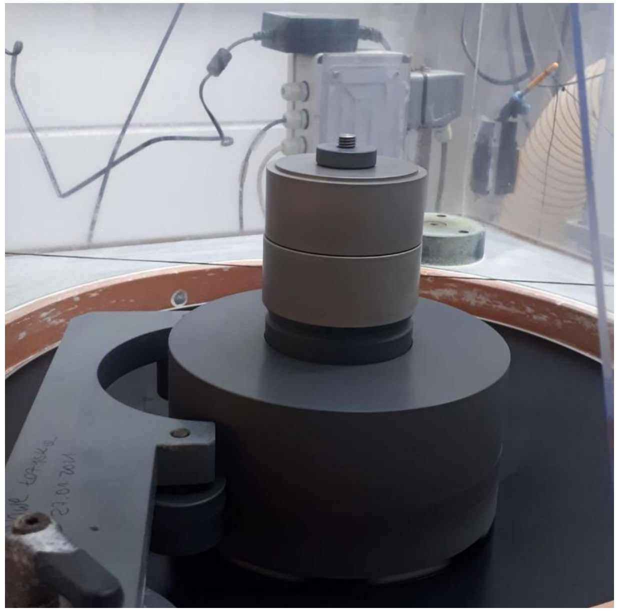


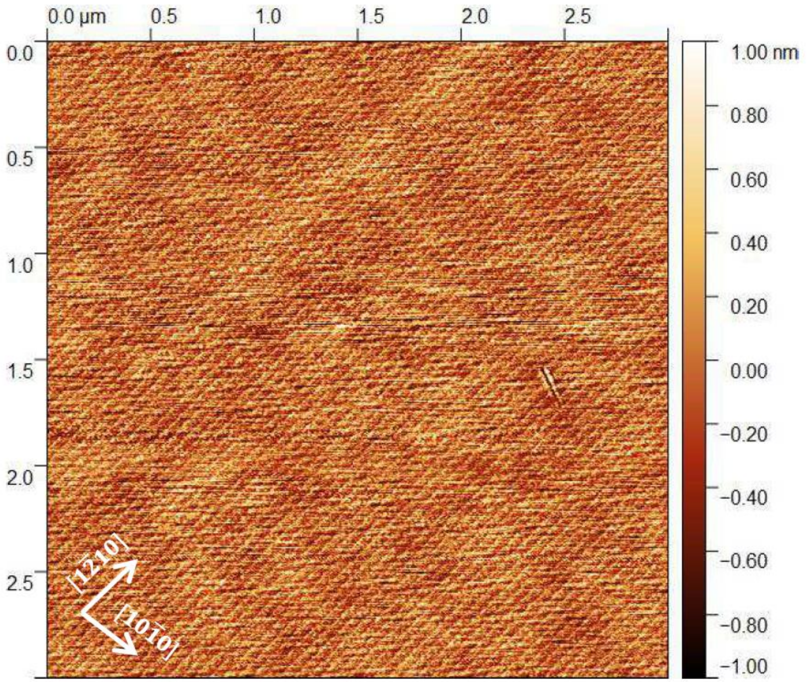


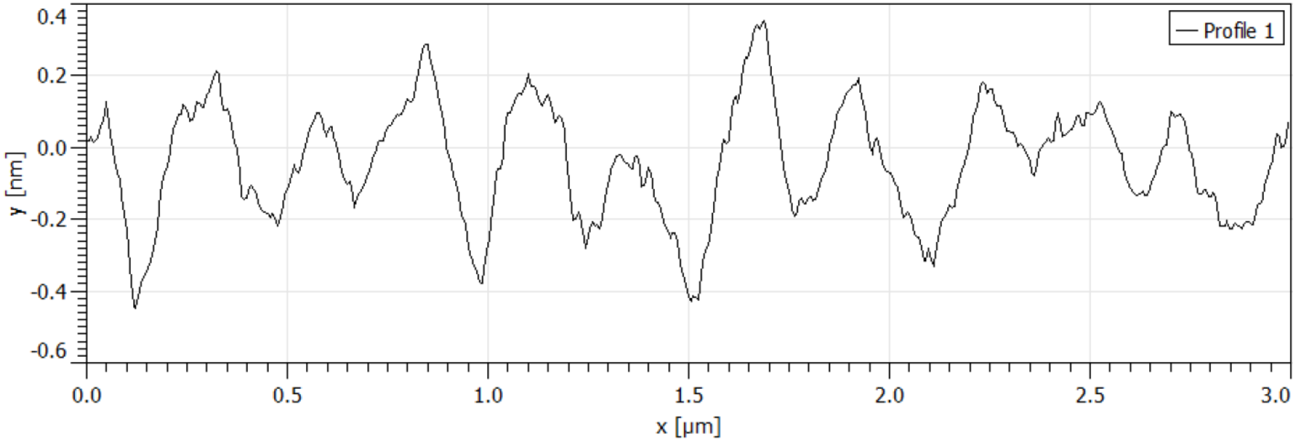
unipress

Wafering Procedures

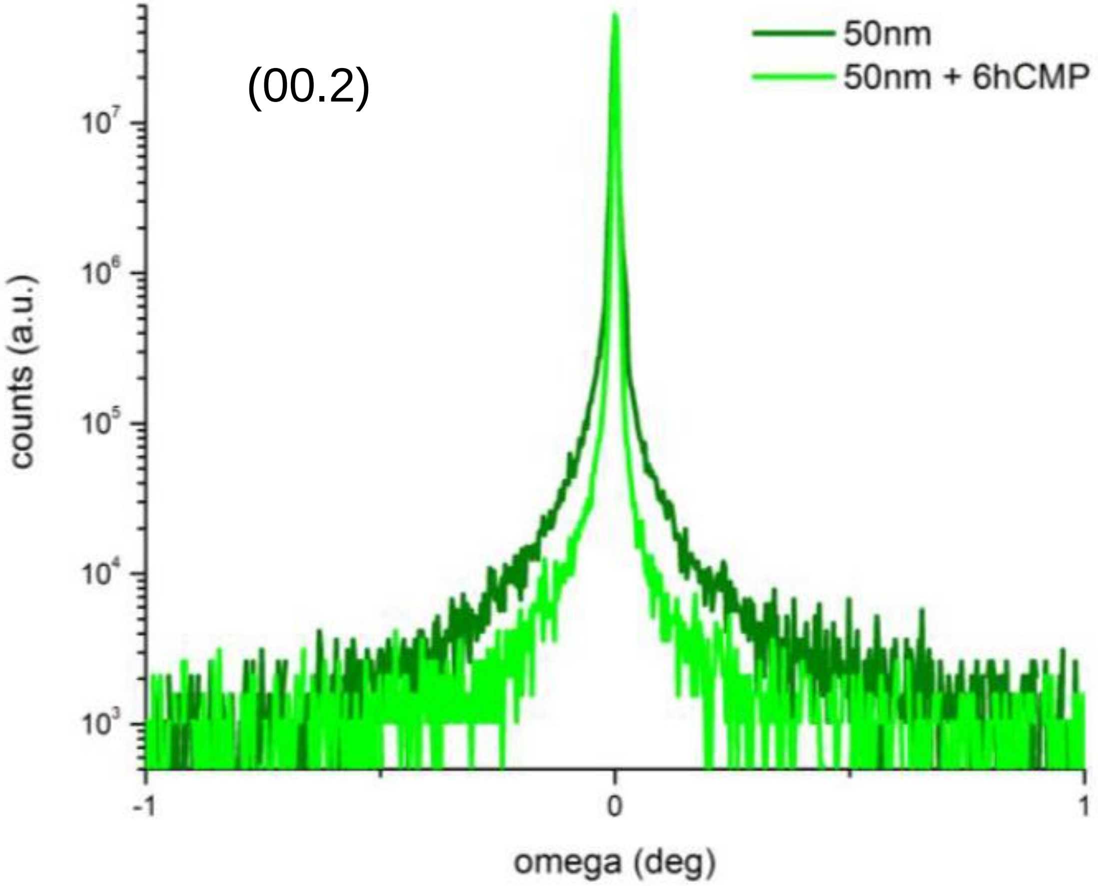


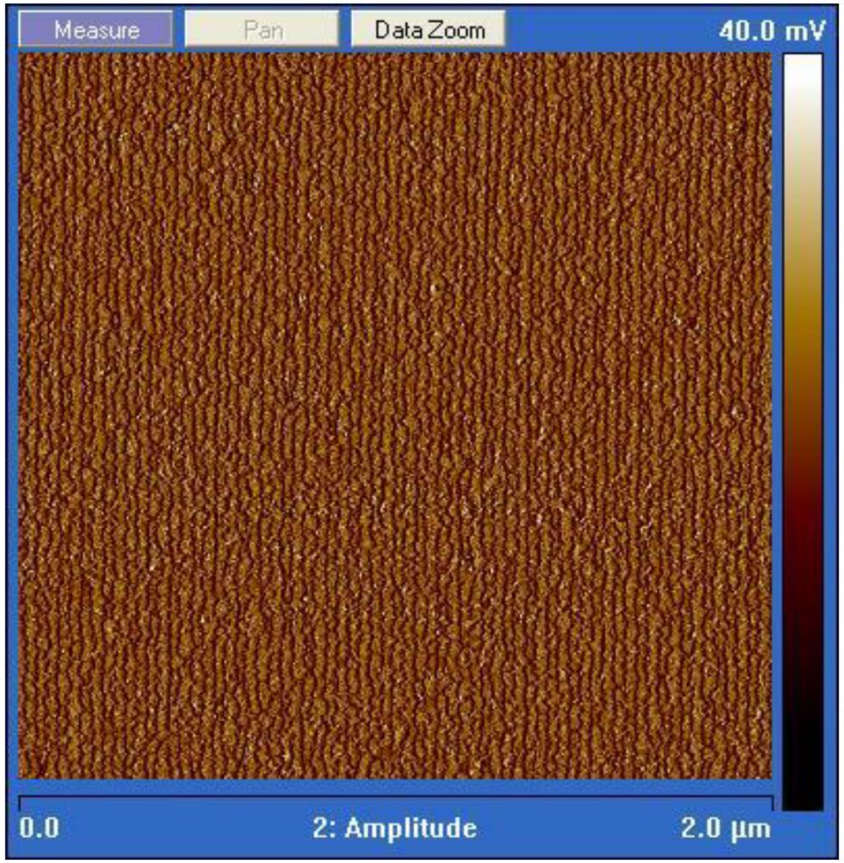






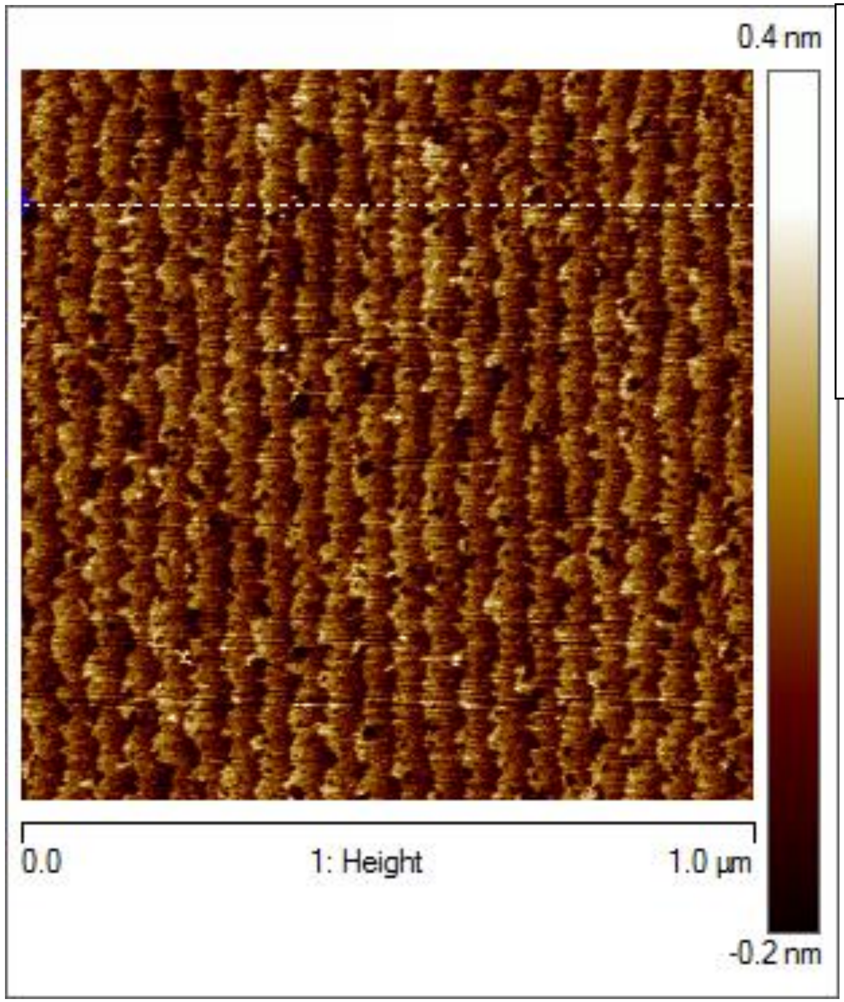
Wafering Procedures

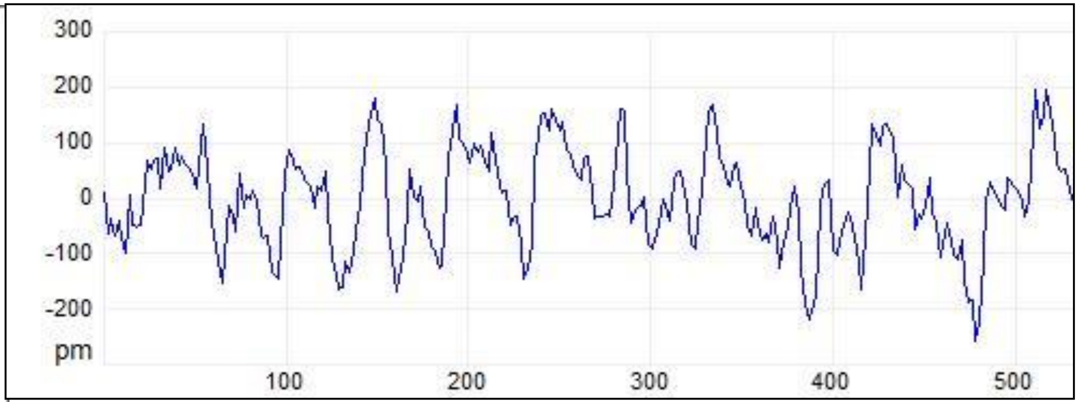




A. Sidor-Żak, M. Fijałkowski, A. Nowakowska-Szkudlarek

Wafering Procedures



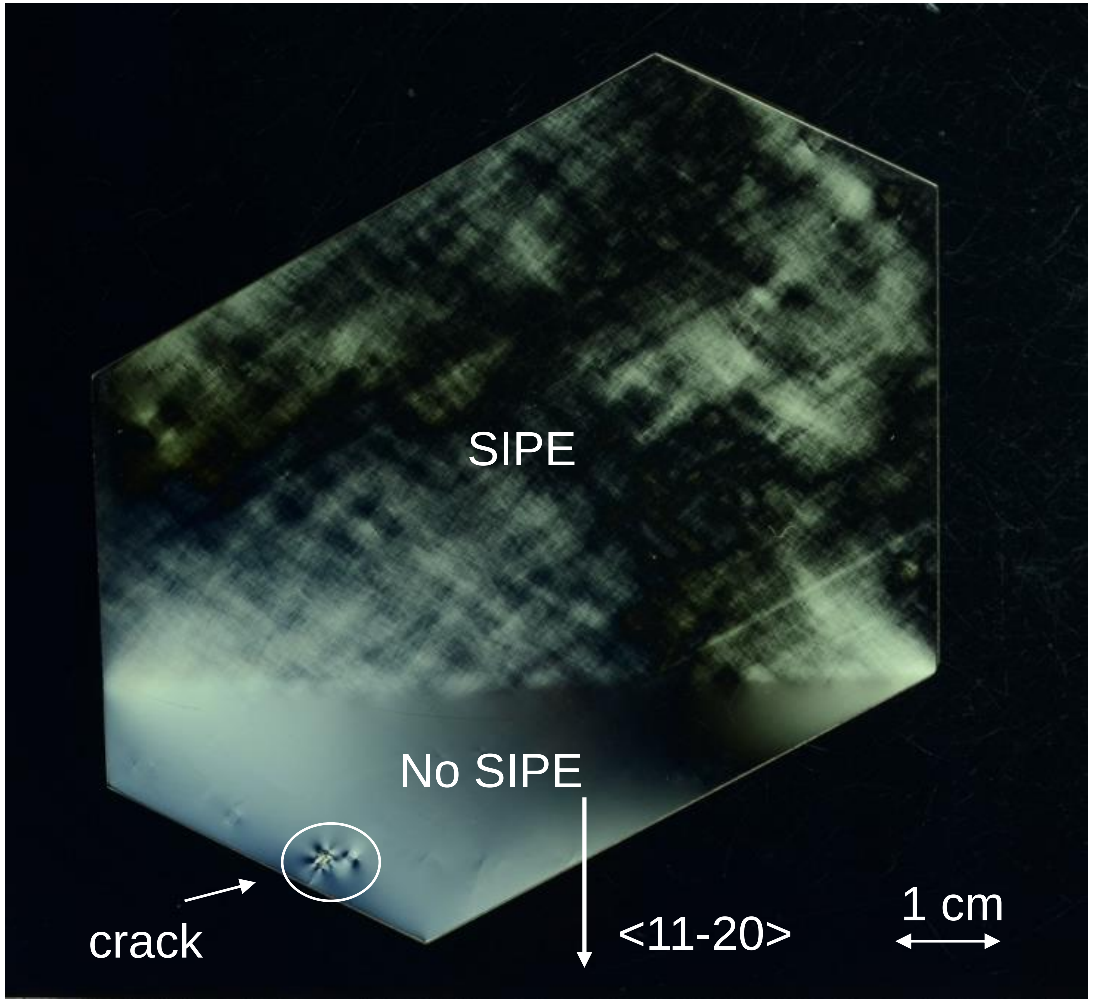


RMS < 0.1 nm

Visible atomic steps

Stress Induced Polarization Effect (SIPE)

- Polariscope (Strain viewer)



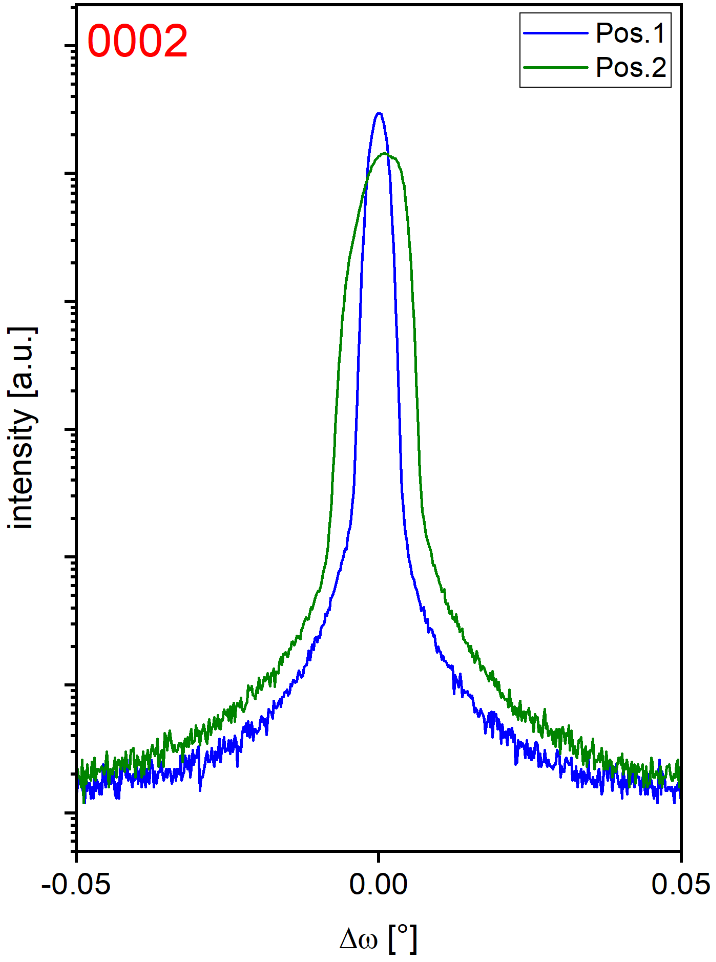
cross-polar

R. Kucharski et al., J. Appl. Phys. 128, 050902 (2020)

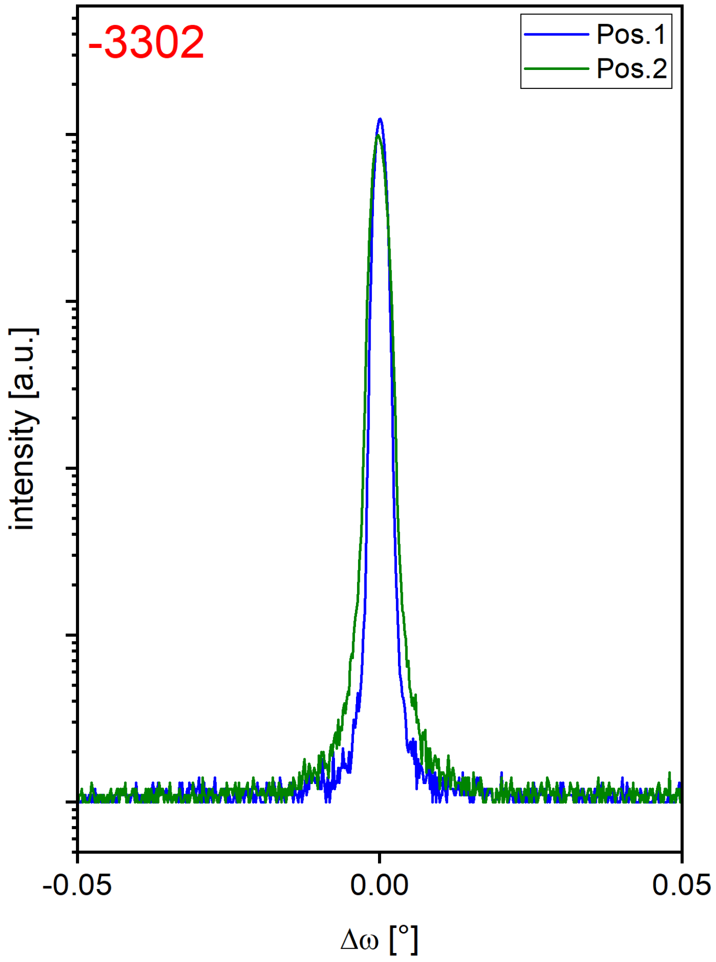
SIPE

- HRXRD: omega scans

Position	Δω 0002 [arcsec]	Δω -3302 [arcsec]
Transparent	10.9	6.8
SIPE	24.6	8.2



measured in skew geometry

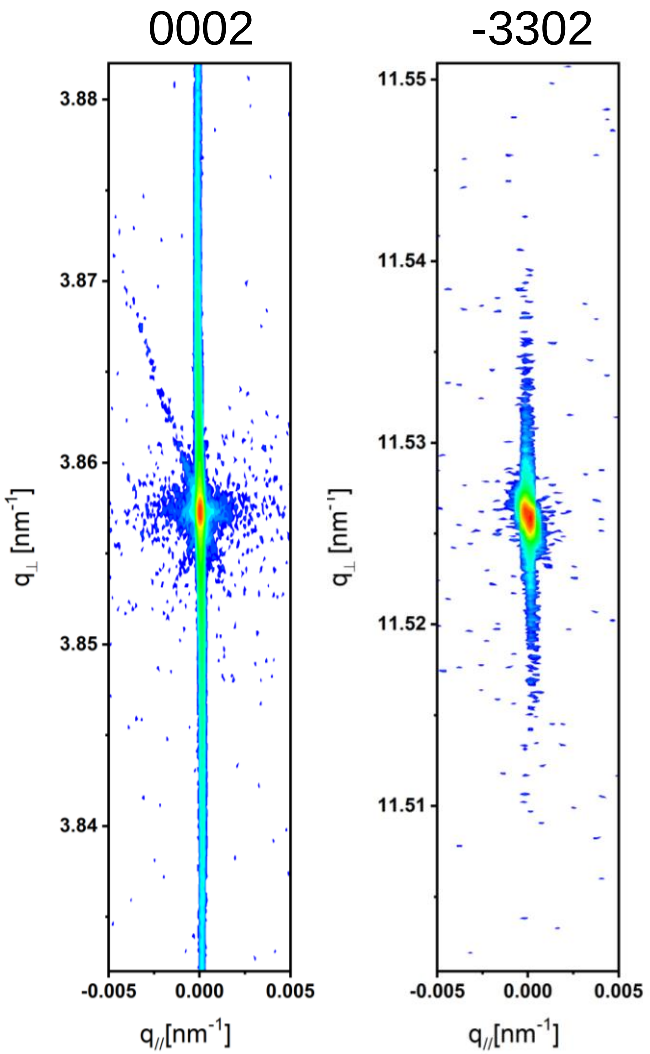


L. Kirste, Fraunhofer IAF

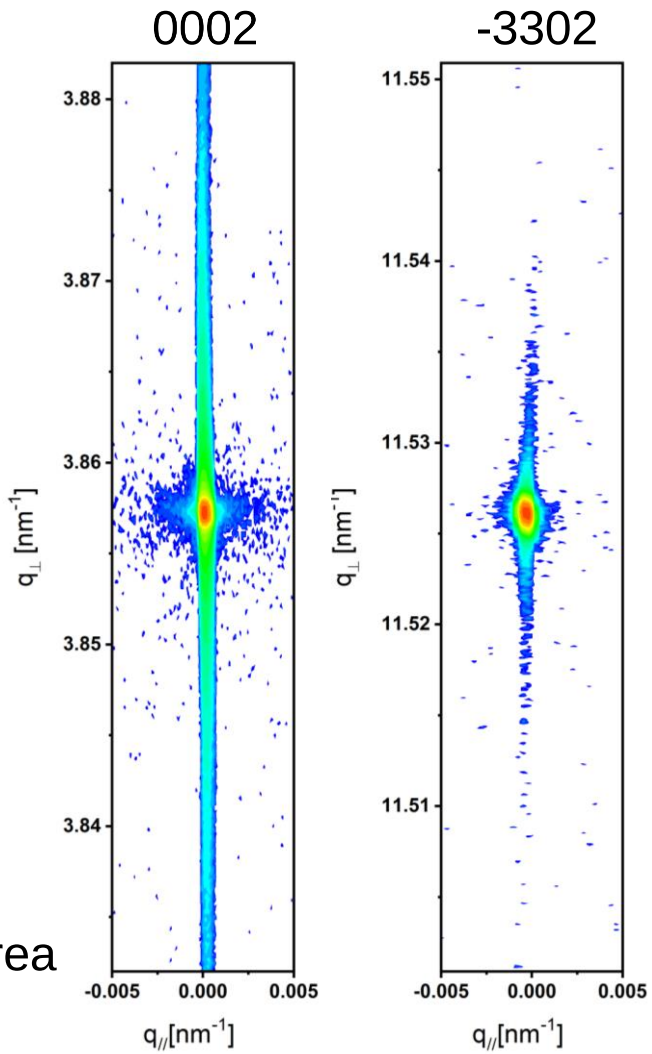
SIPE

- Reciprocal Space Mapping

Transparent area

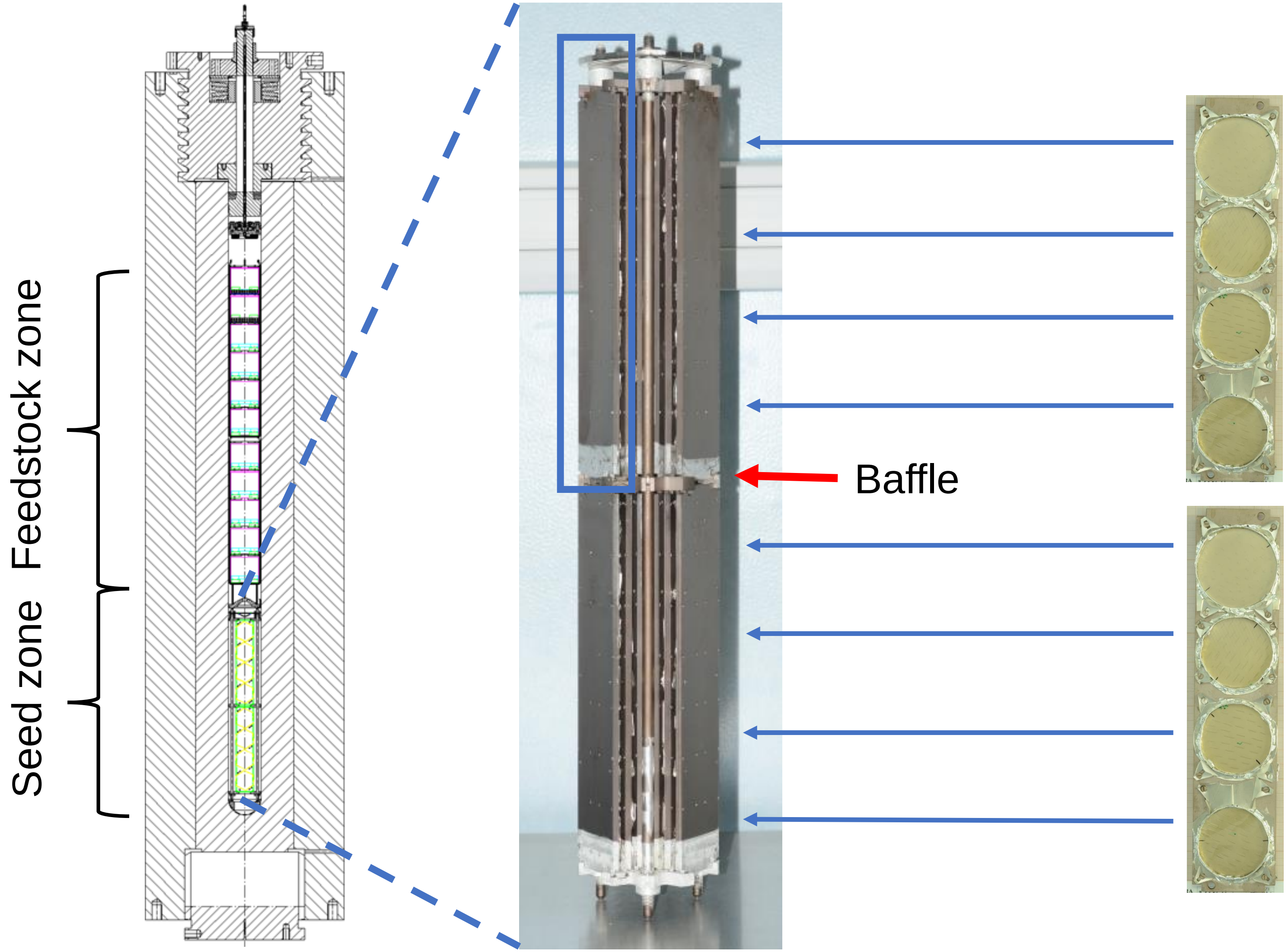


SIPE area



L. Kirste, Fraunhofer IAF

SIPE

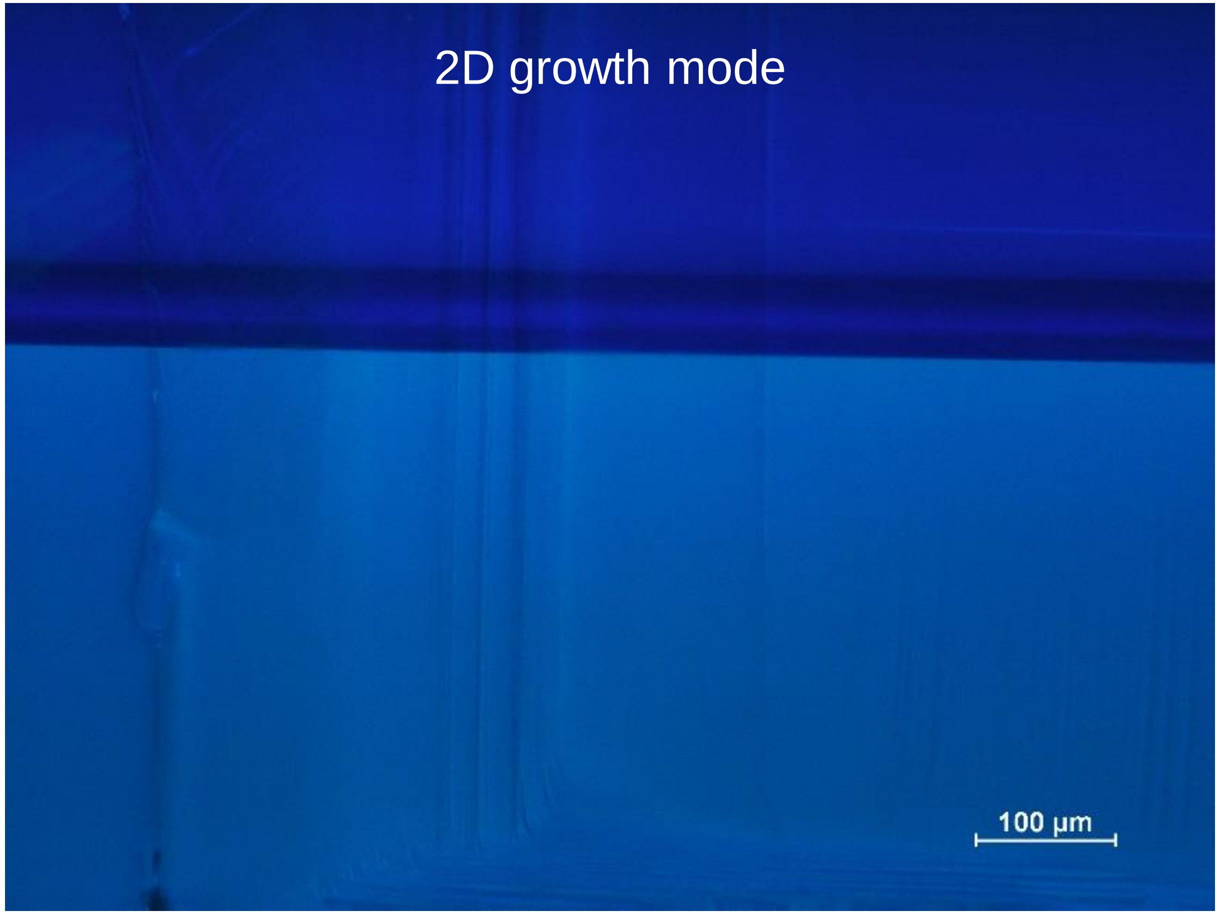


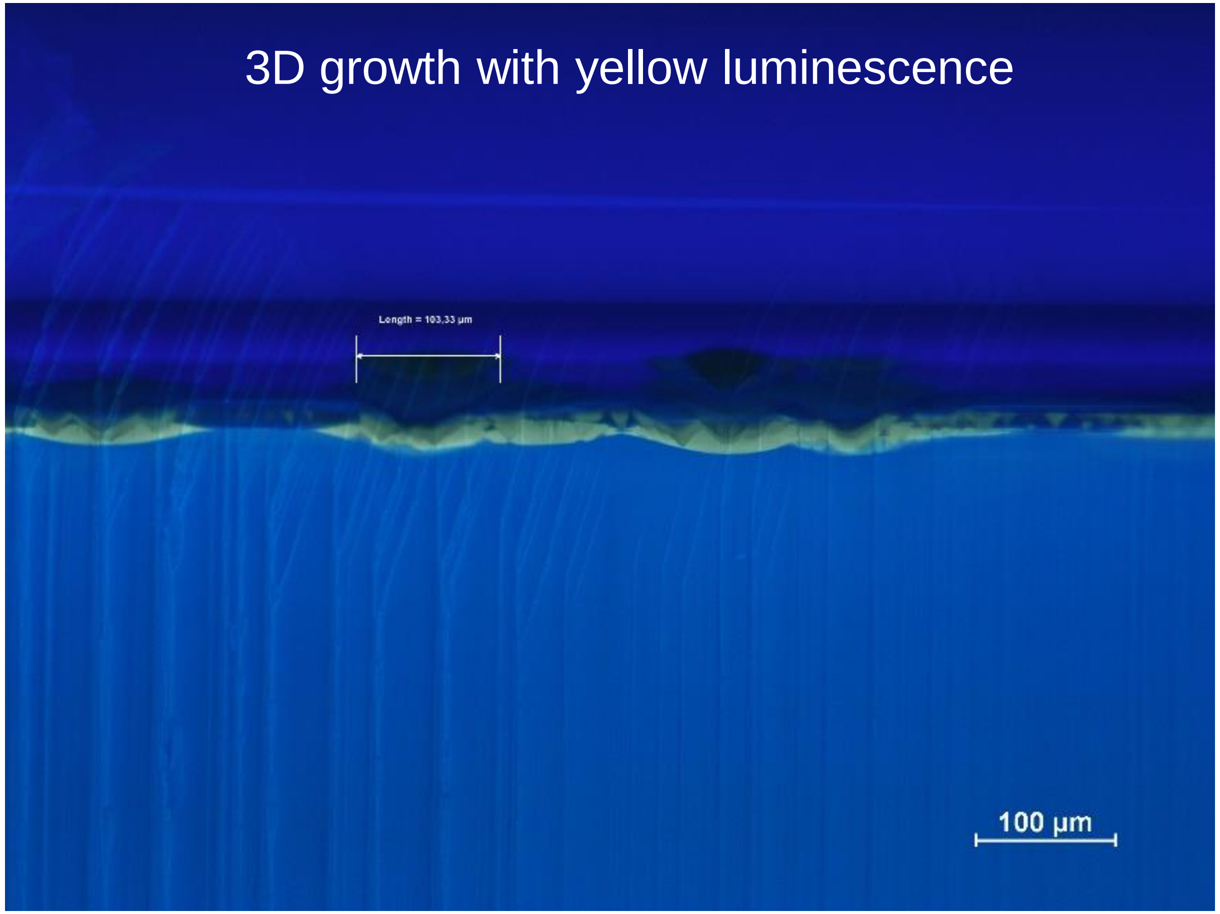
SIPE
22%
19%
26%
34%
Baffle
56%
21%
10%
8%

Analyzed crystals = ~4000

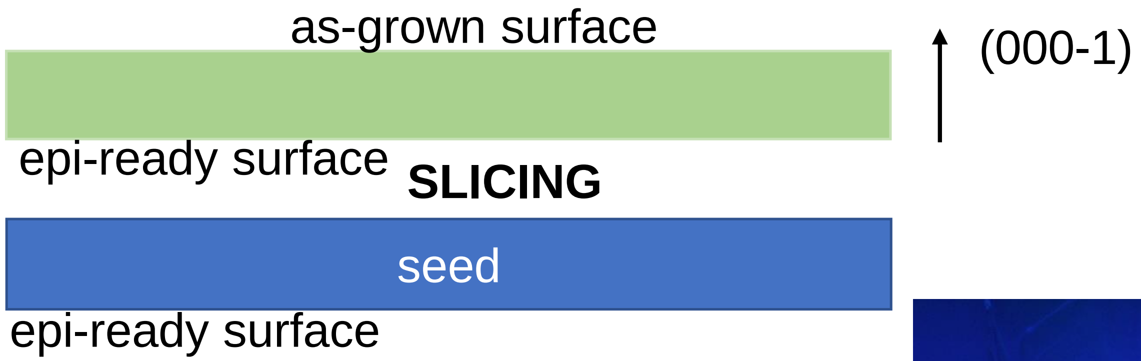
K. Grabianska

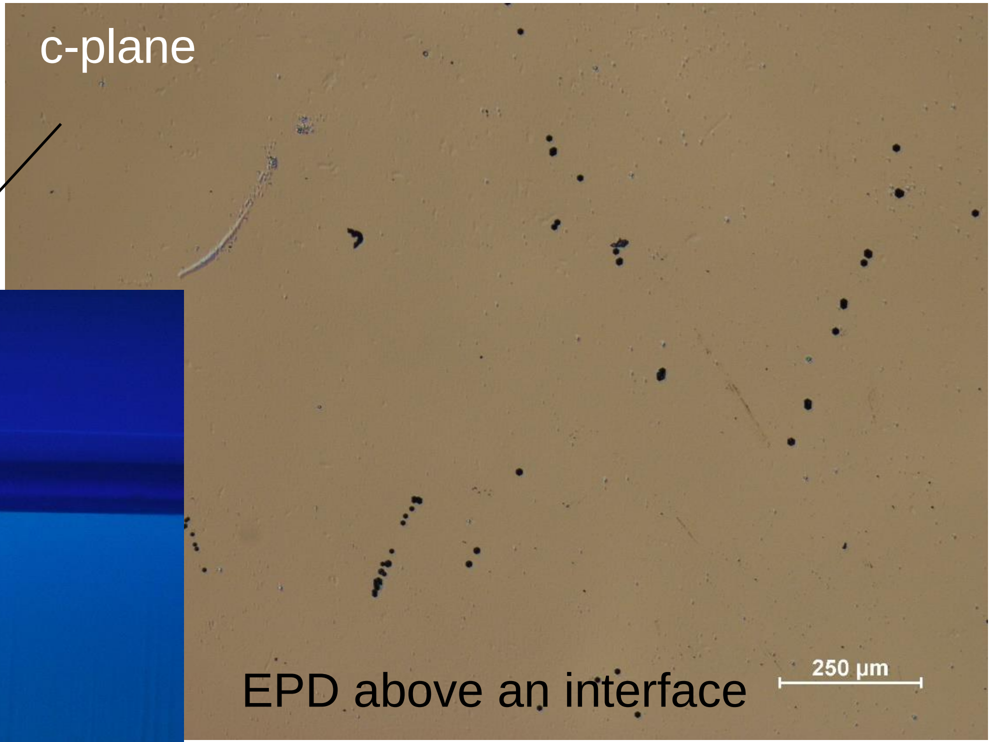
SIPE

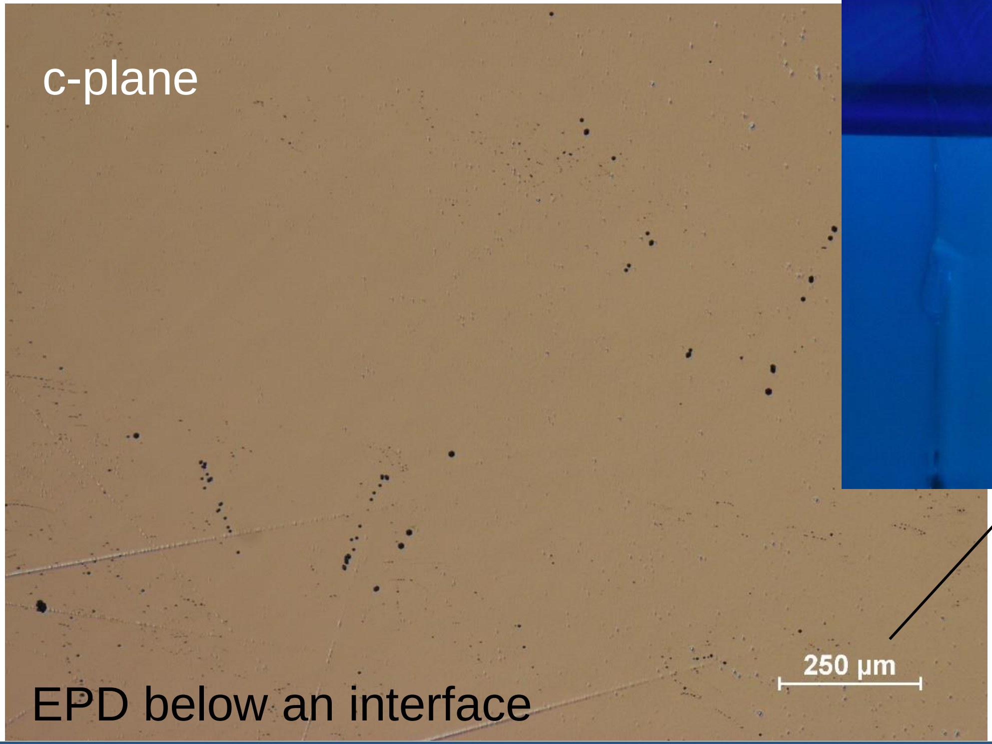


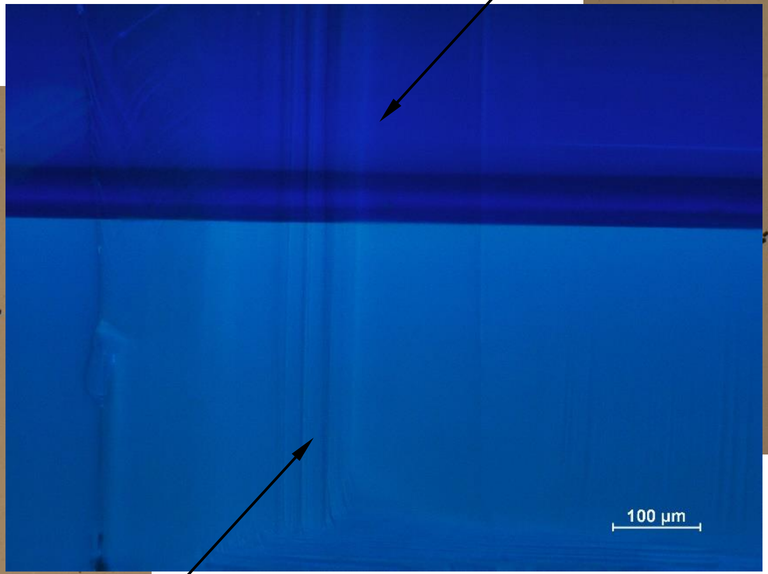


K. Grabianska et al., Crystals 2022, 12, 554









cross-section

Molten KOH+NaOH @450°C

K. Grabianska et al., Crystals 2022, 12, 554

SIPE

as-grown surface

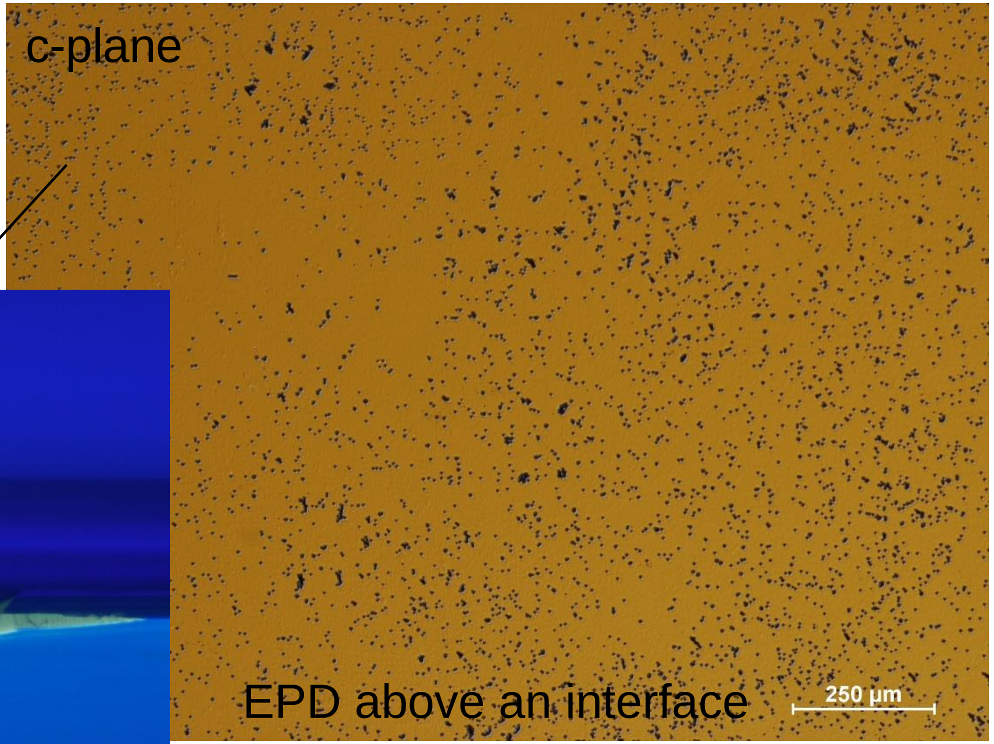
(000-1)

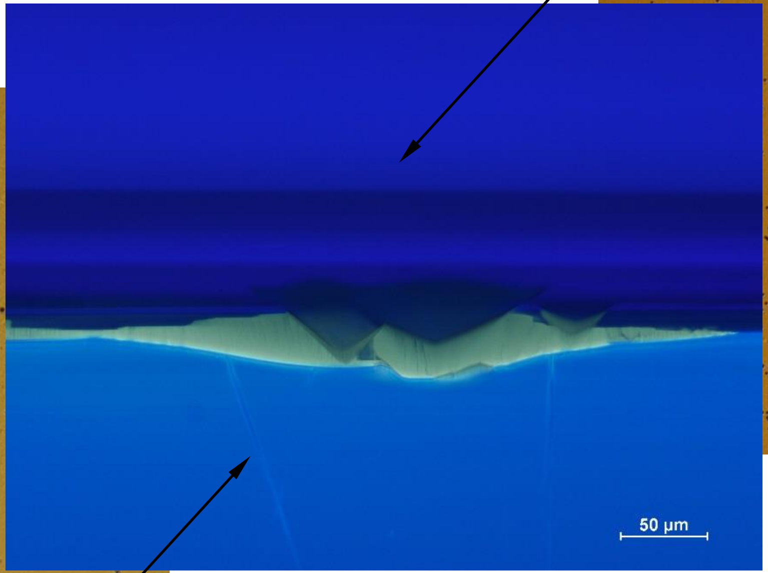
epi-ready surface

SLICING

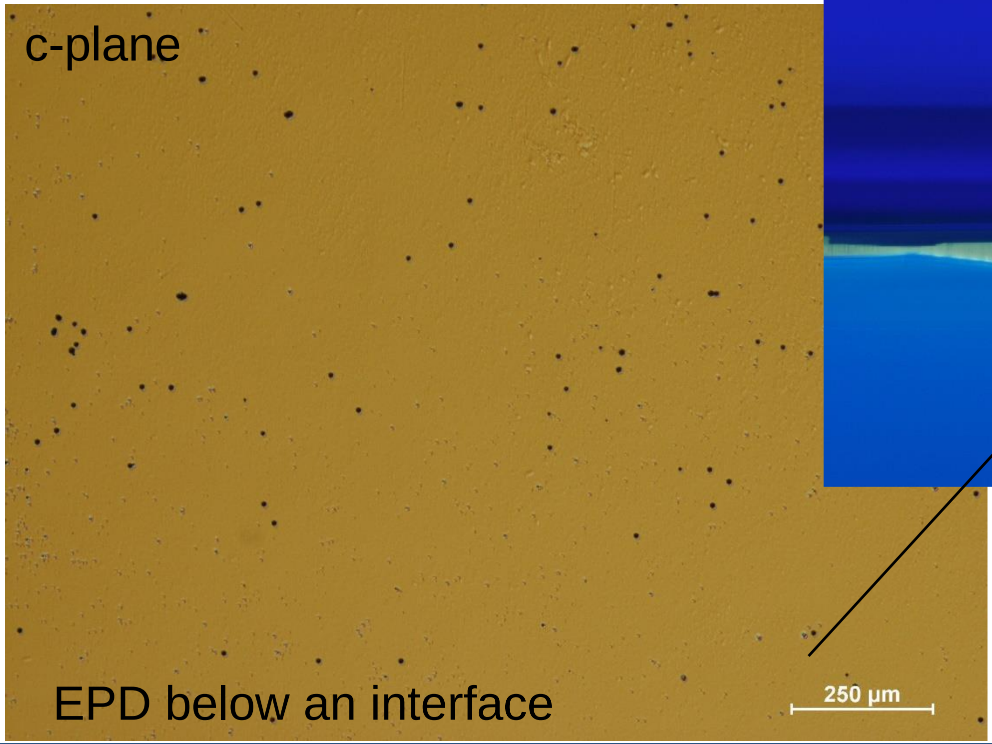
seed

epi-ready surface





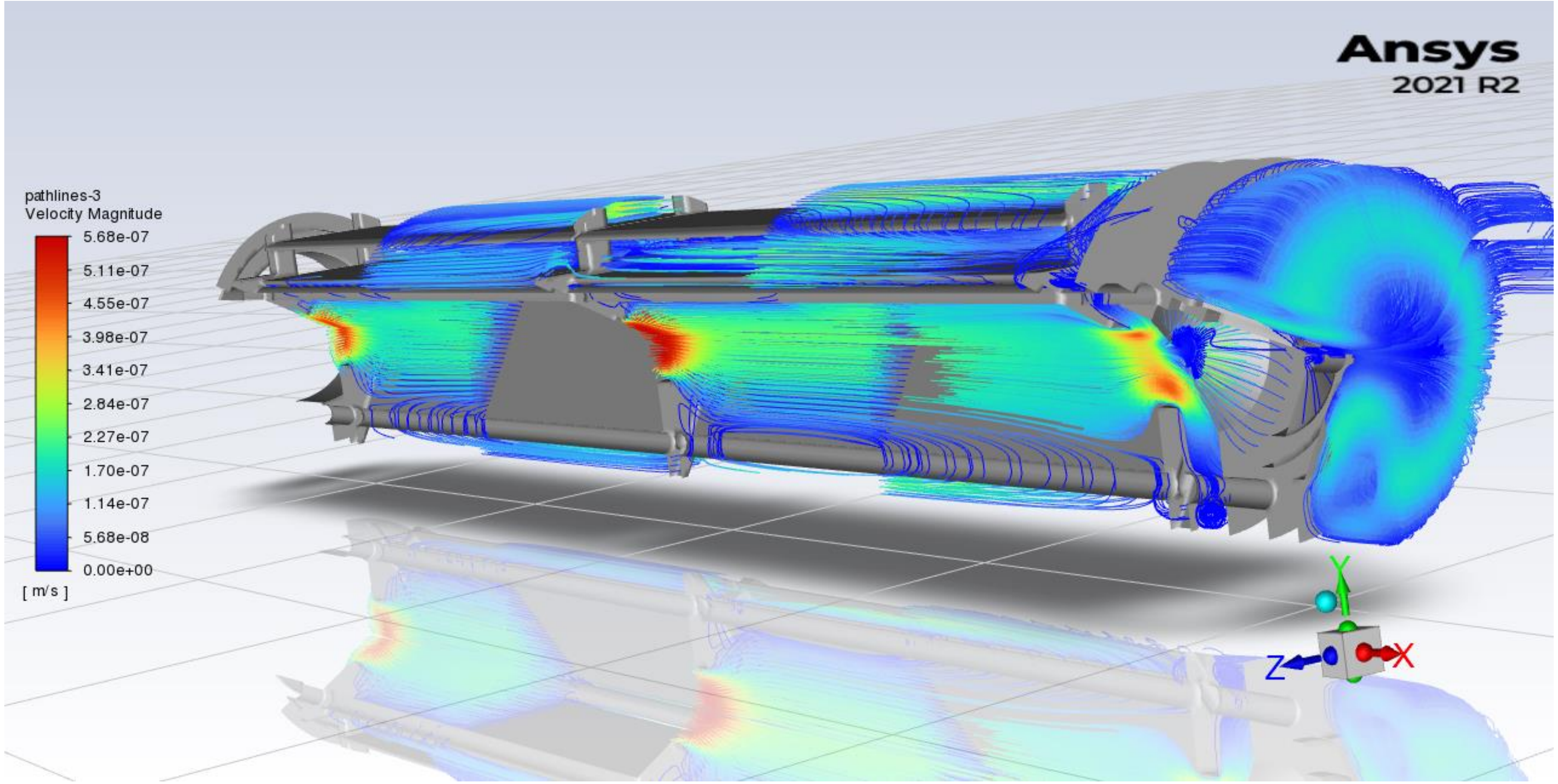
cross-section

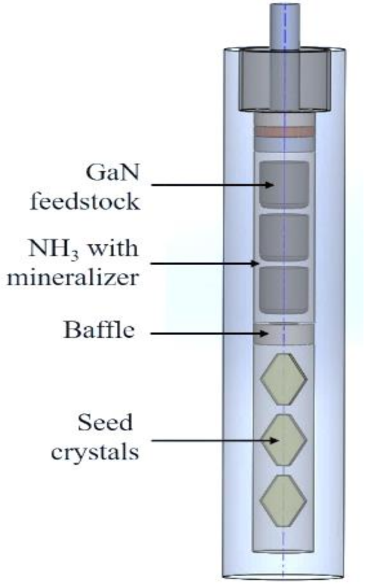


Molten KOH+NaOH @450°C

K. Grabianska et al., Crystals 2022, 12, 554

Modeling of the Convective Transport





- convective flows of reagents

- temperature distribution

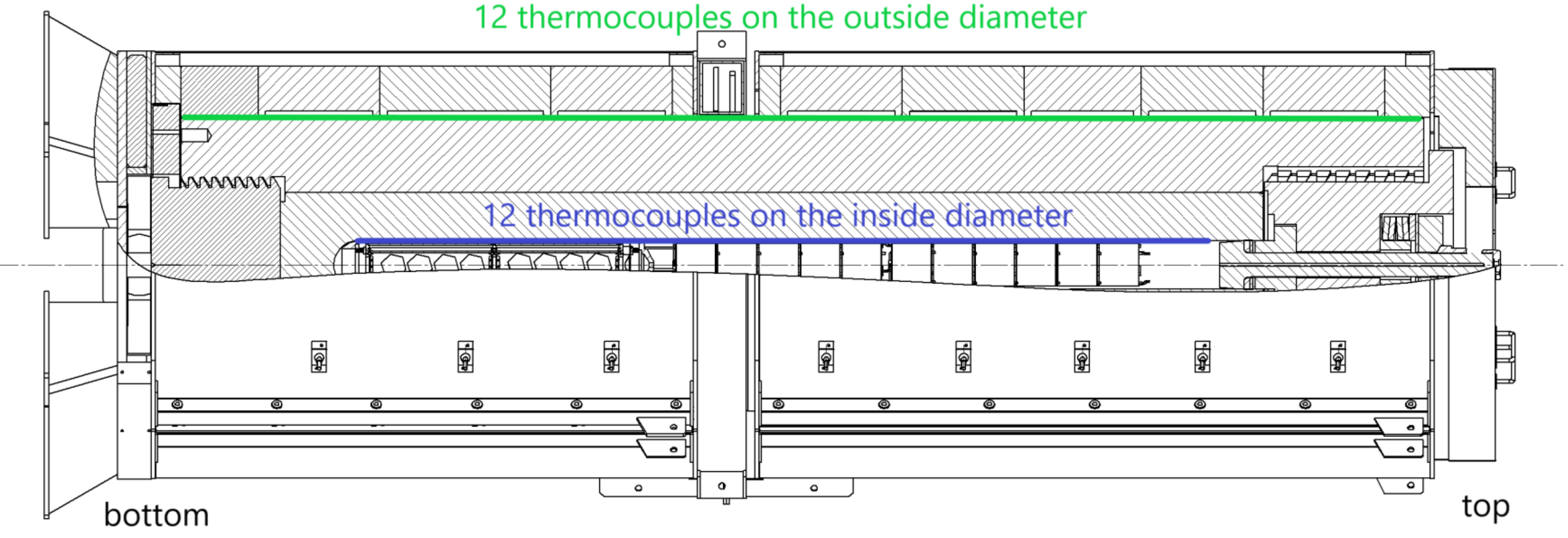
- supersaturation in the crystal growth zone

M. Żak, P. Kempisty, B. Lucznik

Modeling of the Convective Transport

- 24 thermocouples
- Time dependent measurement of thermal process
- Inner wall temperature - 12 thermocouples (B.C. for CFD)

Thermocouple position on the autoclave cross-section



Temperature measurement setup

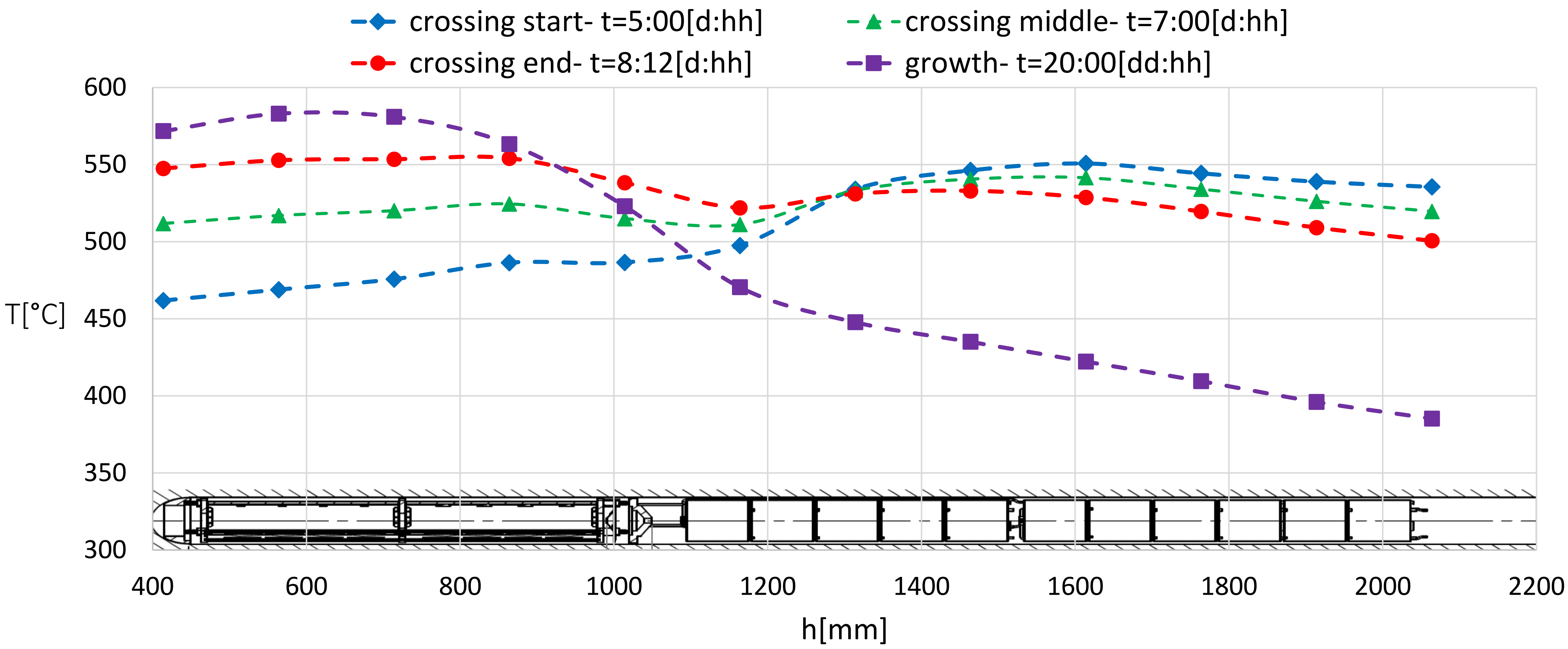
Inside wall thermocouples

M. Żak, P. Kempisty, B. Lucznik

Modeling of the Convective Transport

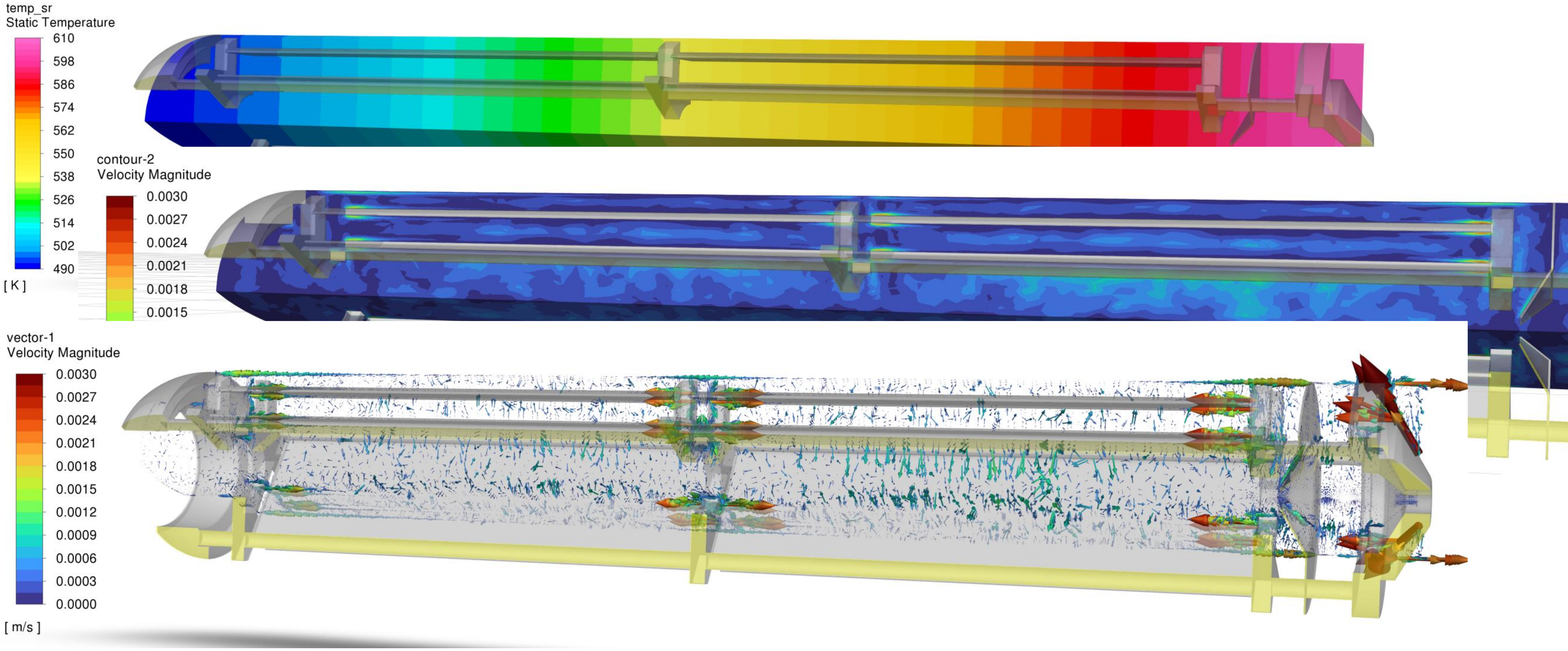
Note: presented temperature profiles were used as boundary conditions

Temperature measured on the inside wall- selected time points



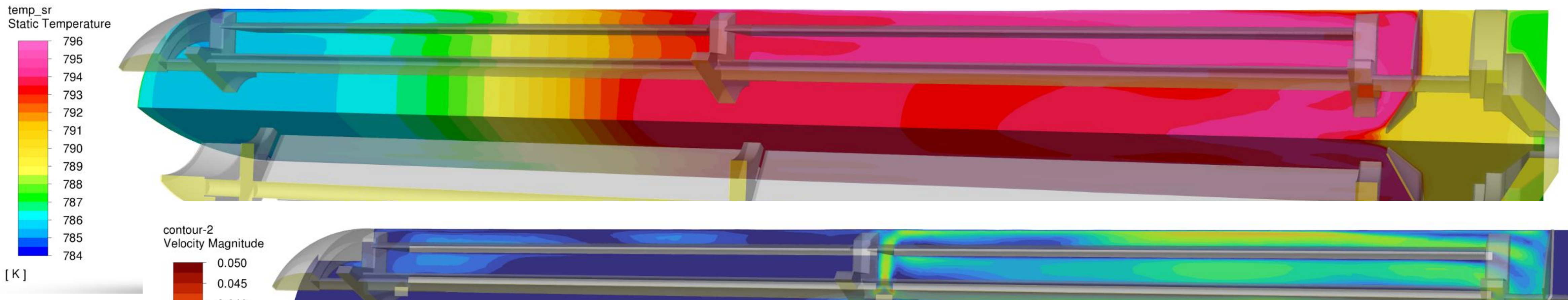
M. Żak, P. Kempisty, B. Lucznik

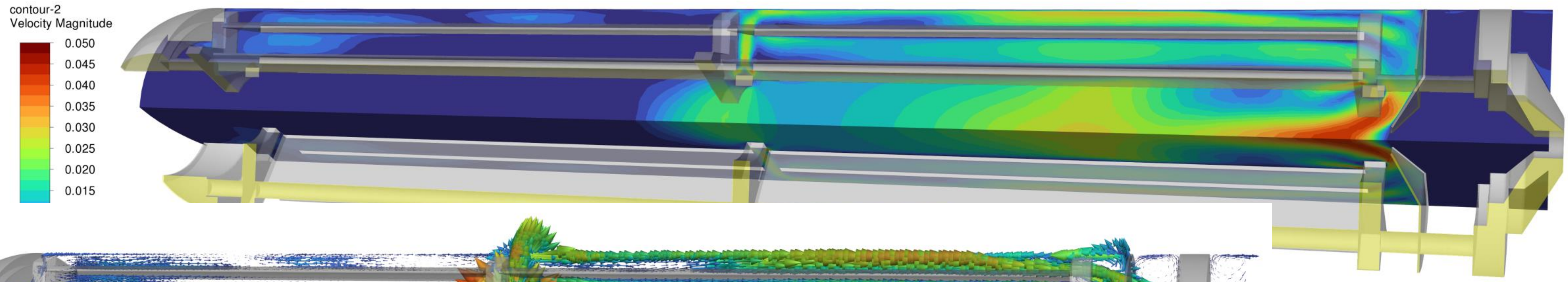
Convective Flow – Back Etching

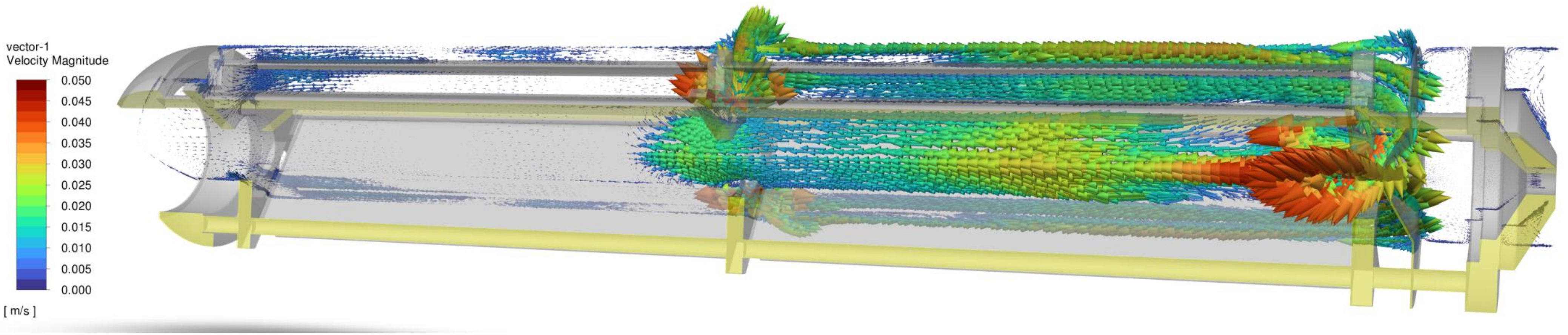


M. Zak

Convective Flow – Temperature Transition



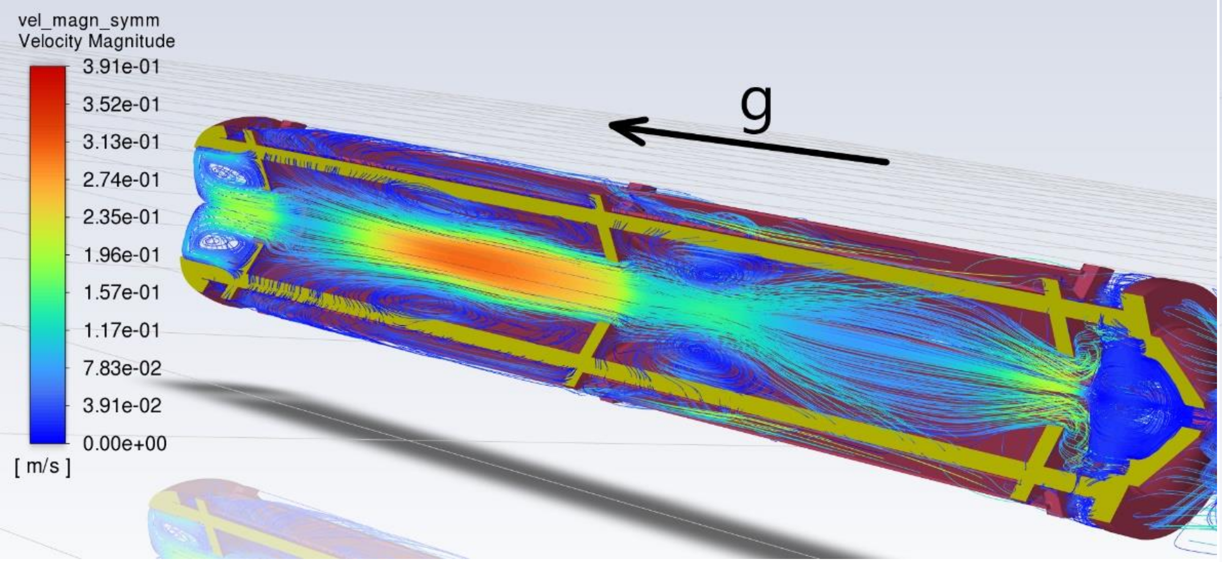




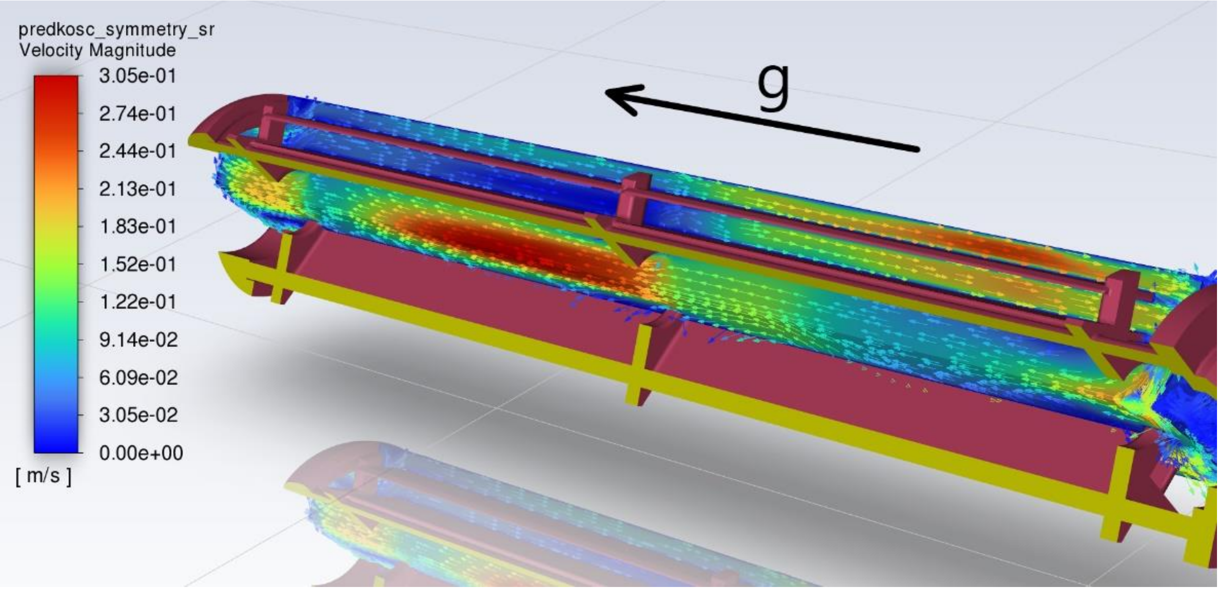
M. Zak

Convective Flow – Growth Stage

- Velocities in the NH_3 solution vary from a few cm/s to 30 cm/s (turbulent flow!)



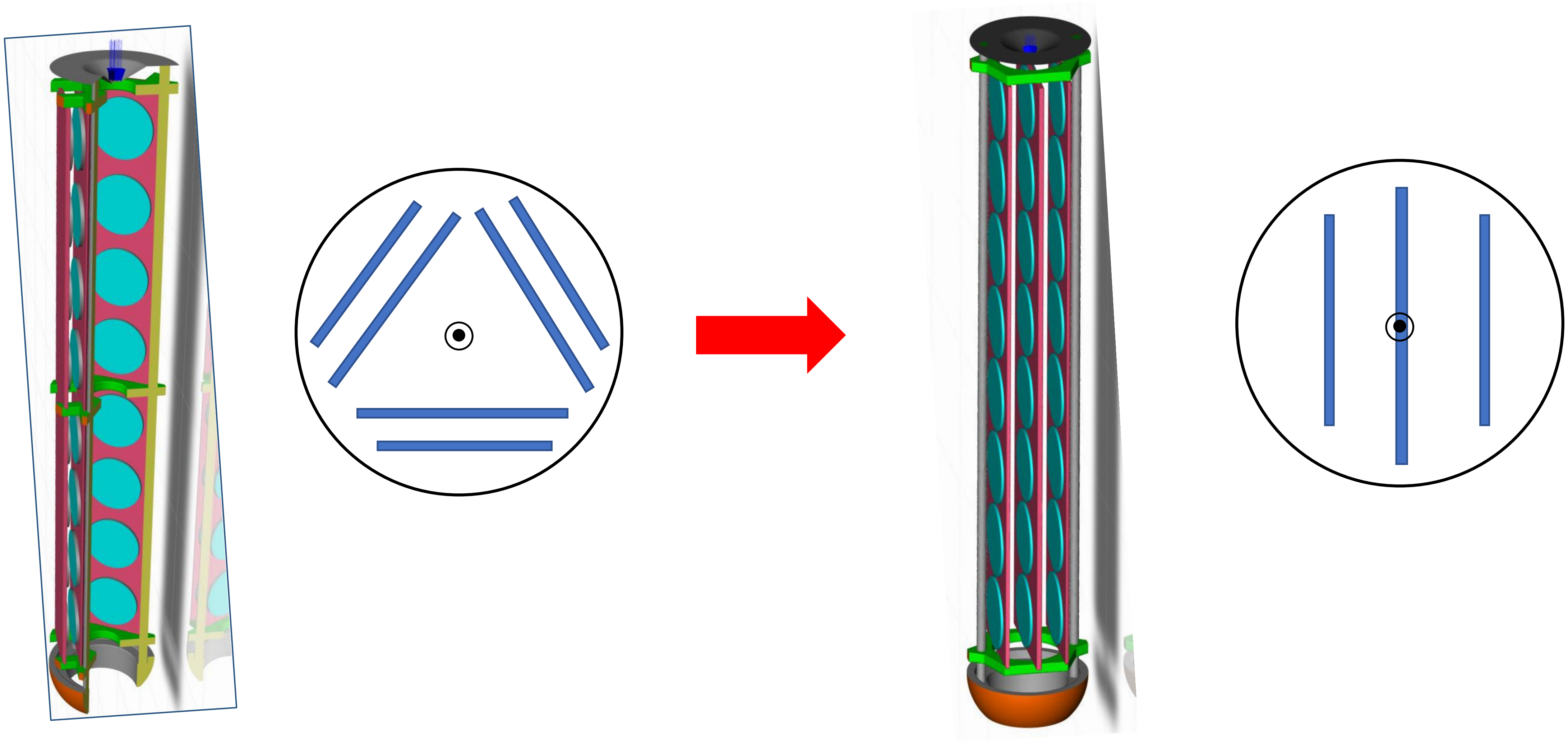
Velocity magnitude on streamlines
in the crystal growth zone



Distribution of velocity magnitude and vectors
in the crystal growth zone

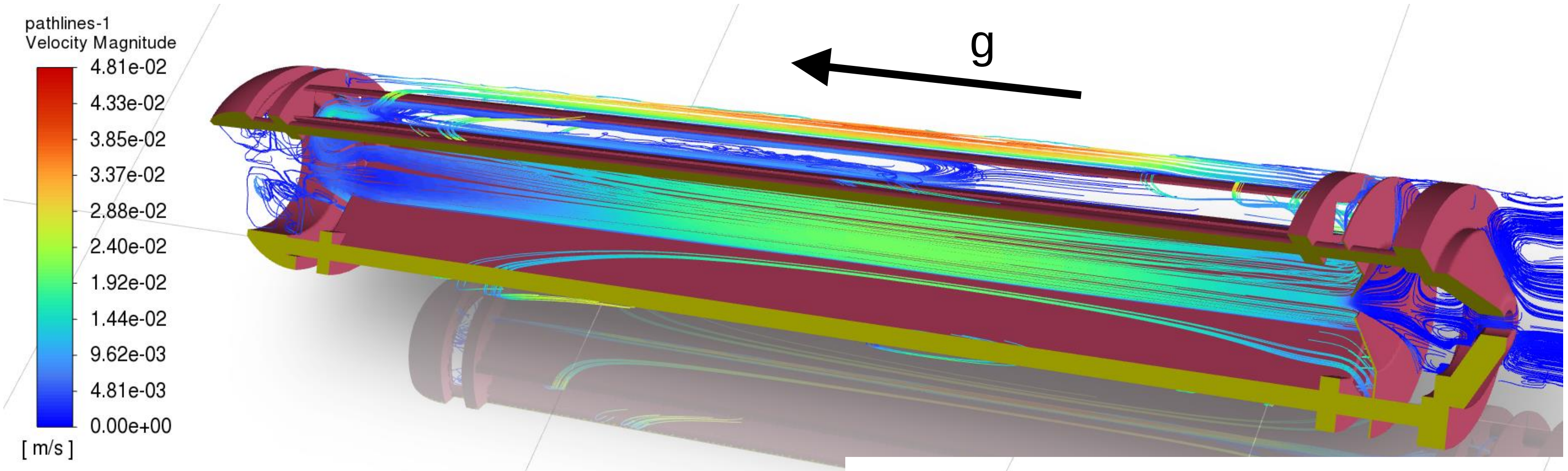
M. Zak

Convective flow – New Installation



R. Kucharski, B. Lucznik, M. Zak

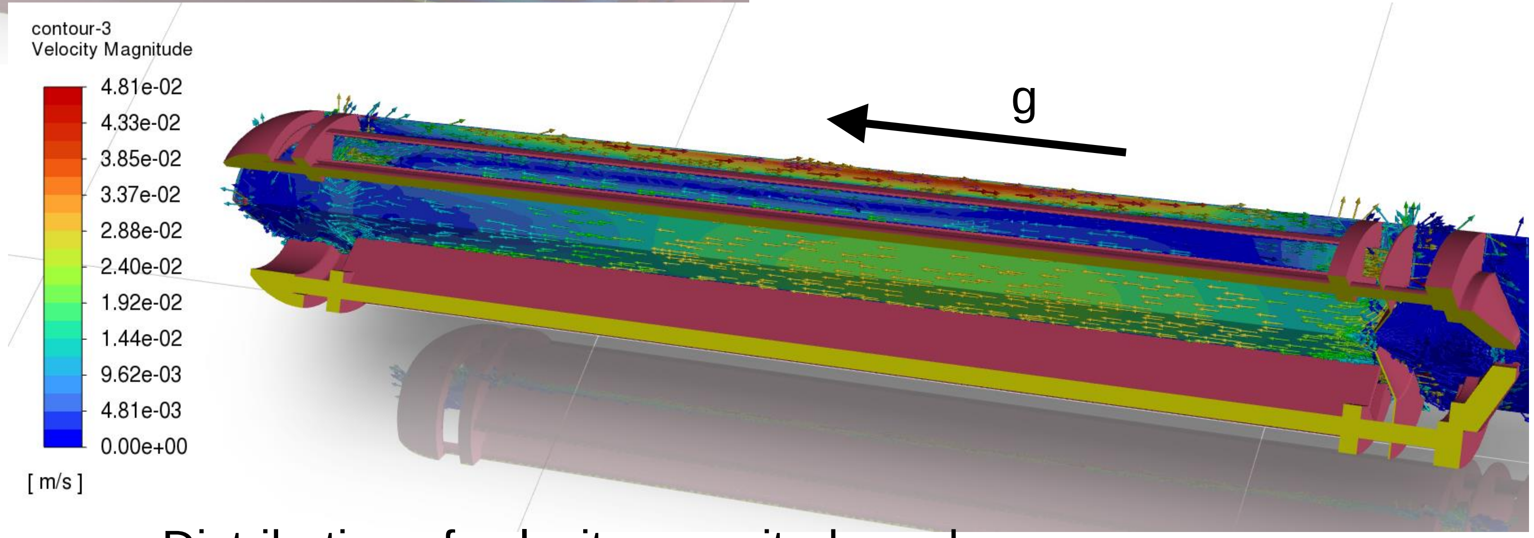
Convective flow



Velocity magnitude on streamlines in the crystal growth zone

Laminar flow

Velocity ~ 2-5 cm/sec

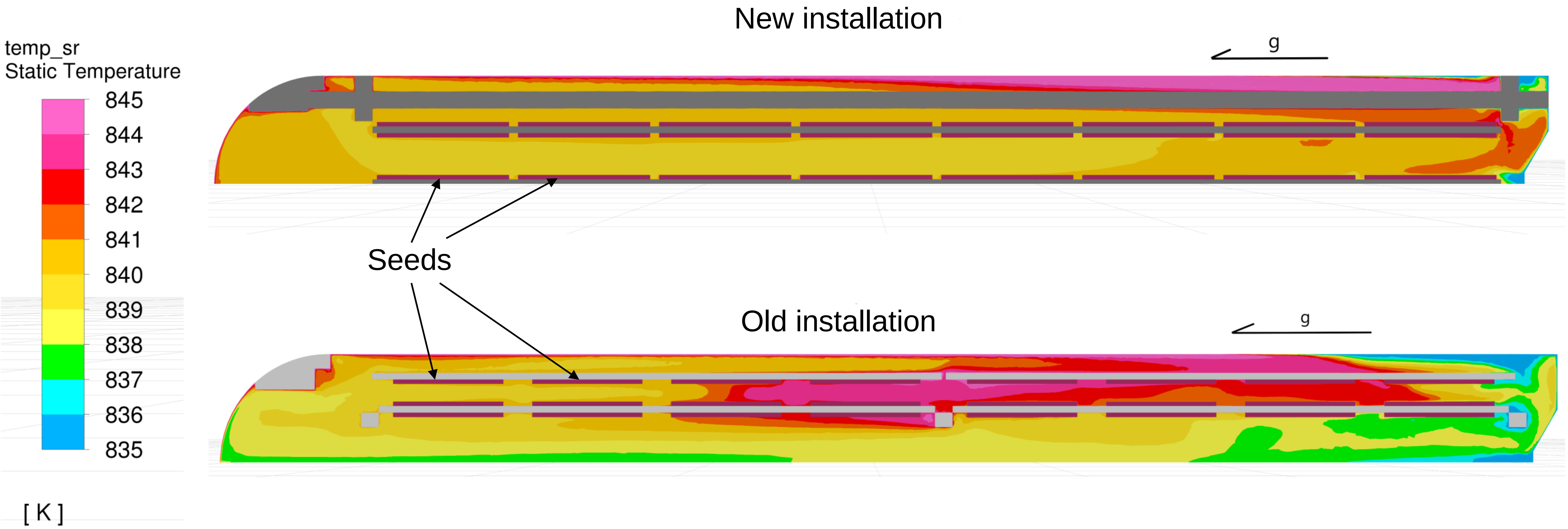


Distribution of velocity magnitude and vectors in the growth zone

M. Żak, P. Kempisty

Convective Flow – Fluid Temperature Distribution

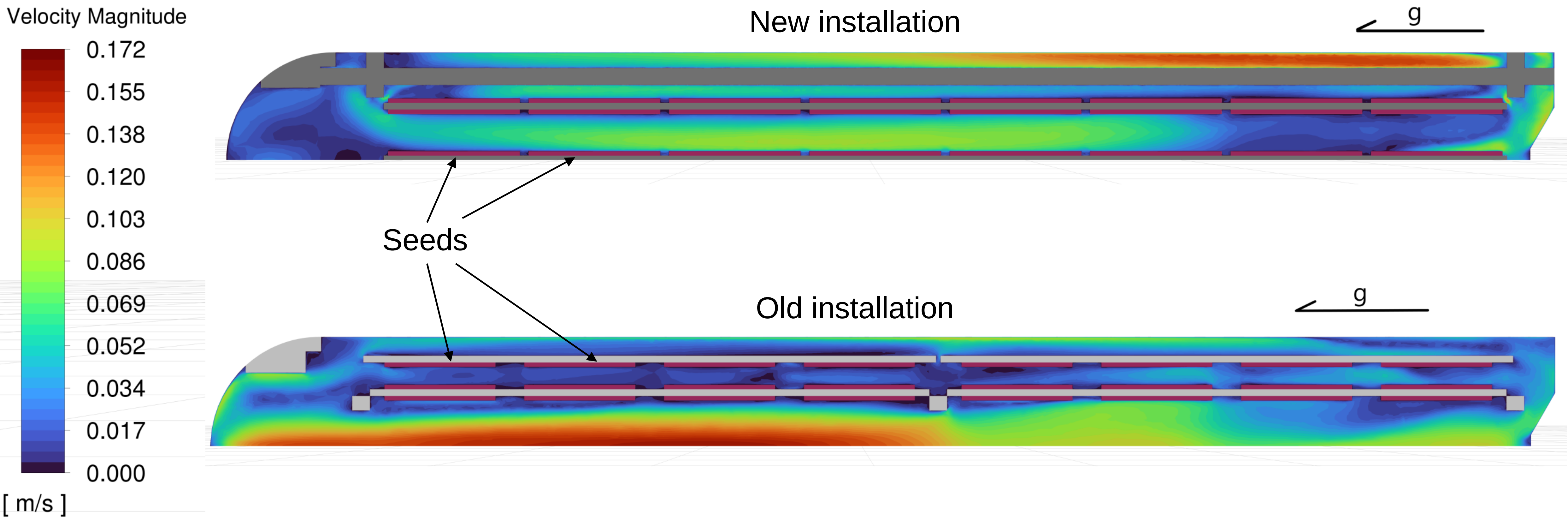
- Temperature is more evenly distributed in new installation



M. Zak

Convective Flow – Velocity Magnitude Distribution

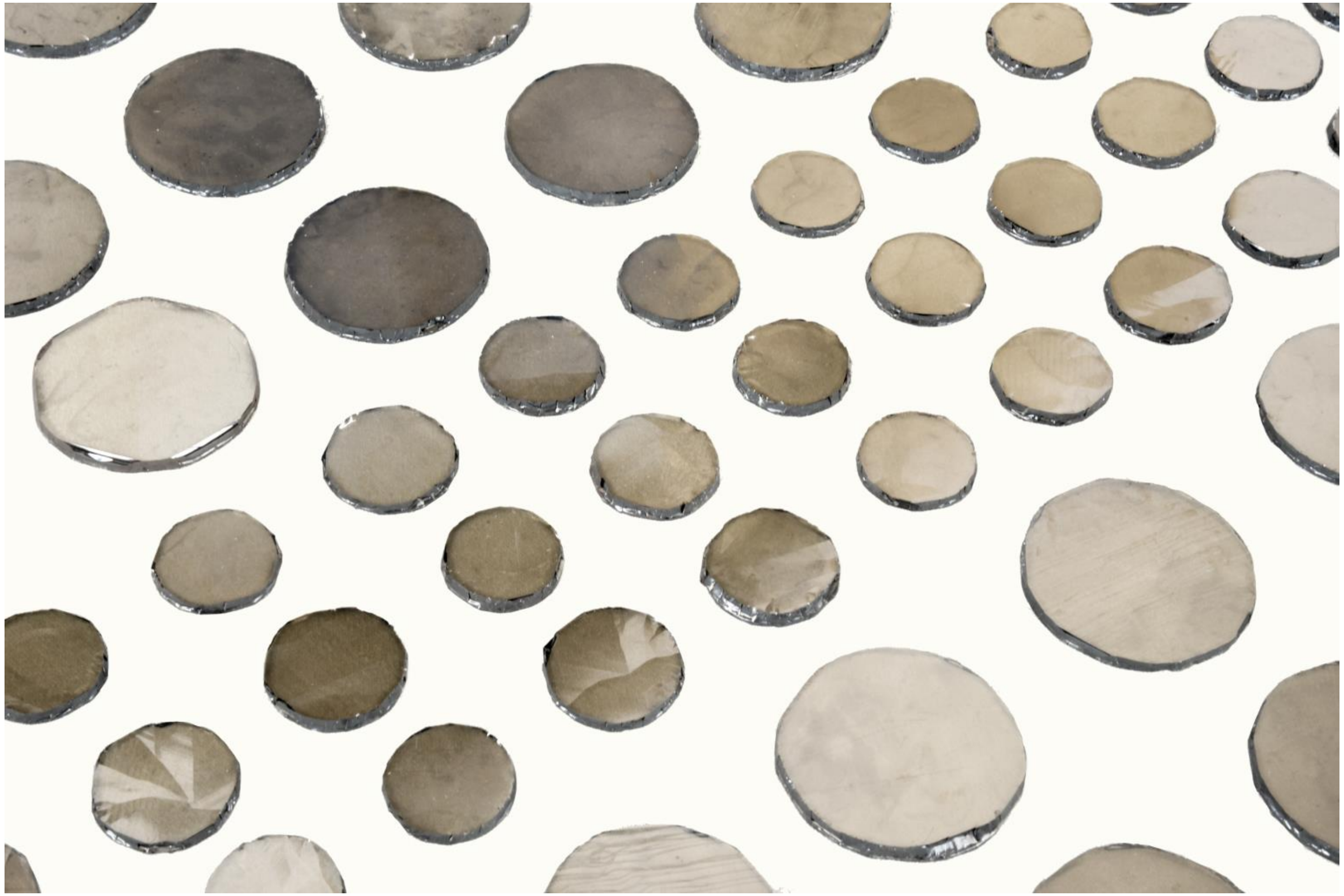
- Velocity maximum value is lower in new installation
- Velocity magnitude is more evenly distributed in new installation



M. Zak

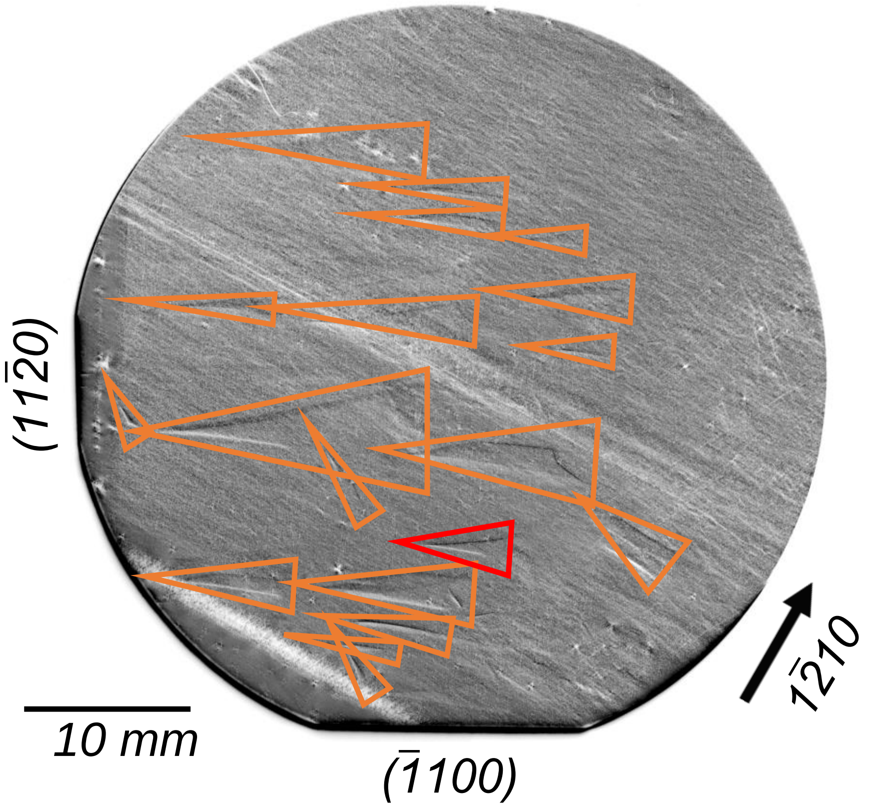
Morphology of Ammonothermal GaN Crystals

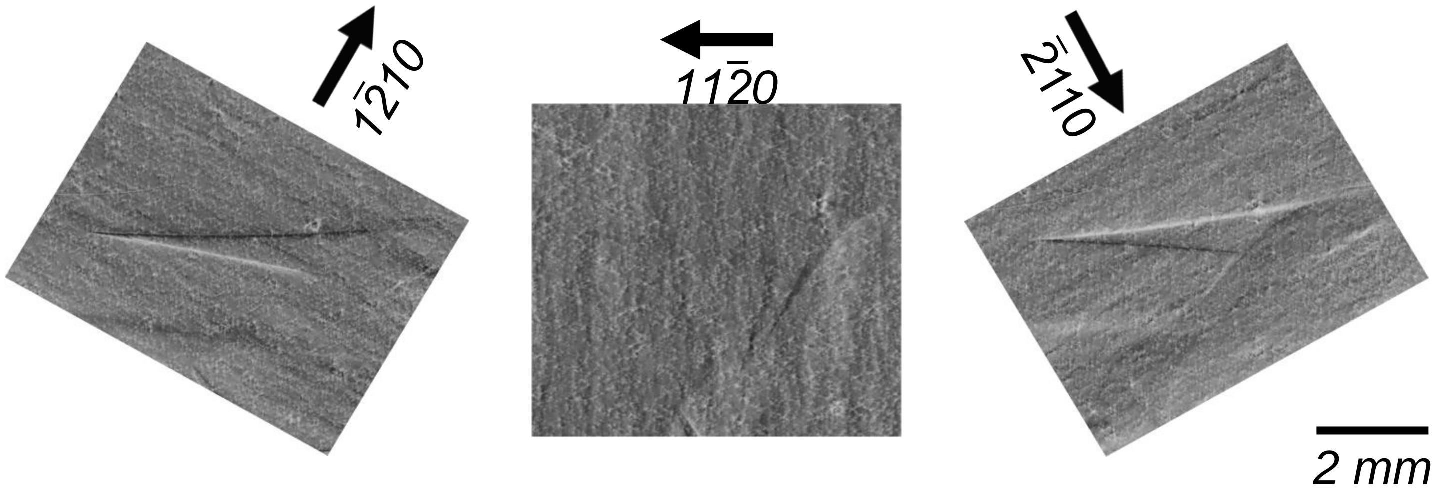
- More uniform crystal morphology
- No new SIPE



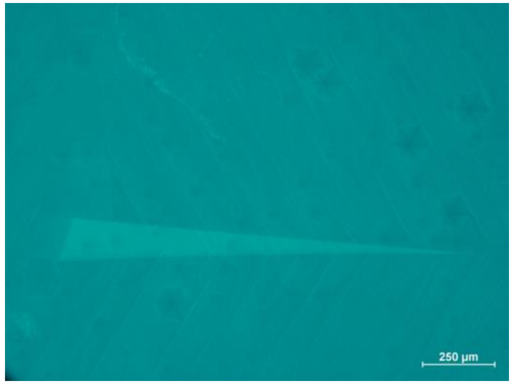
Ammonothermal GaN Substrates – Surface Defects

- Carrot (Propeller) Defects





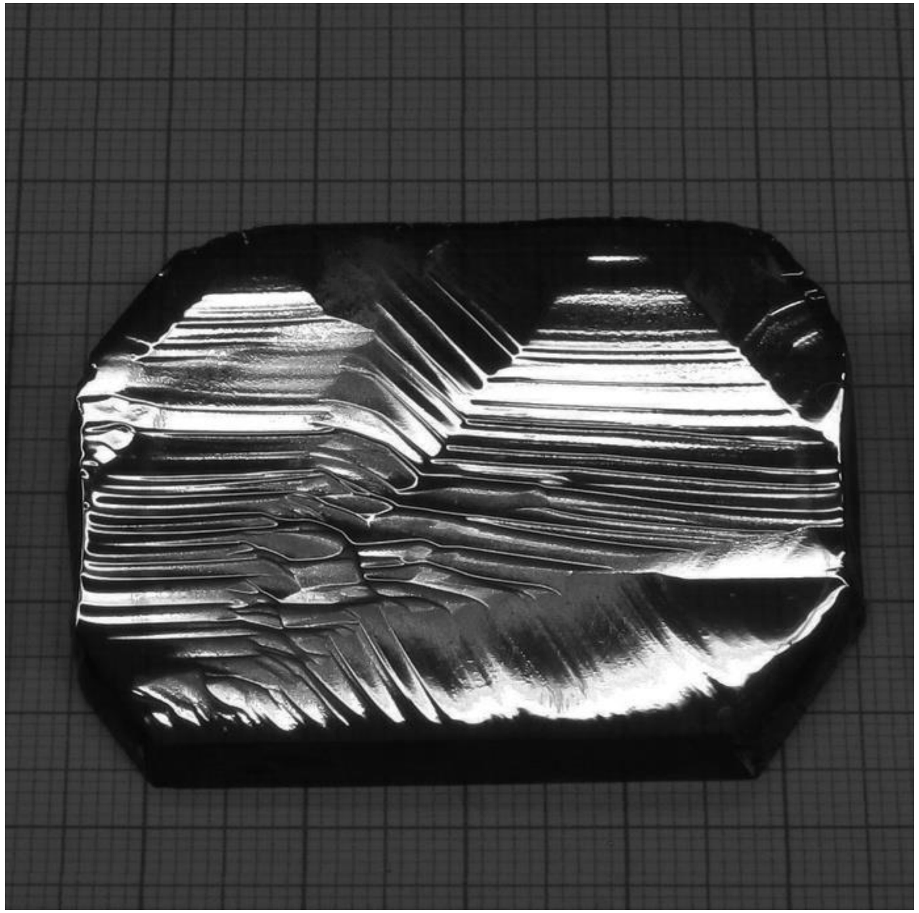
➔ Planar defects related to facets that show triangular contrasts caused by a slight bending of the reflecting planes along the boundaries and results from a small difference of lattice parameters in adjacent regions.

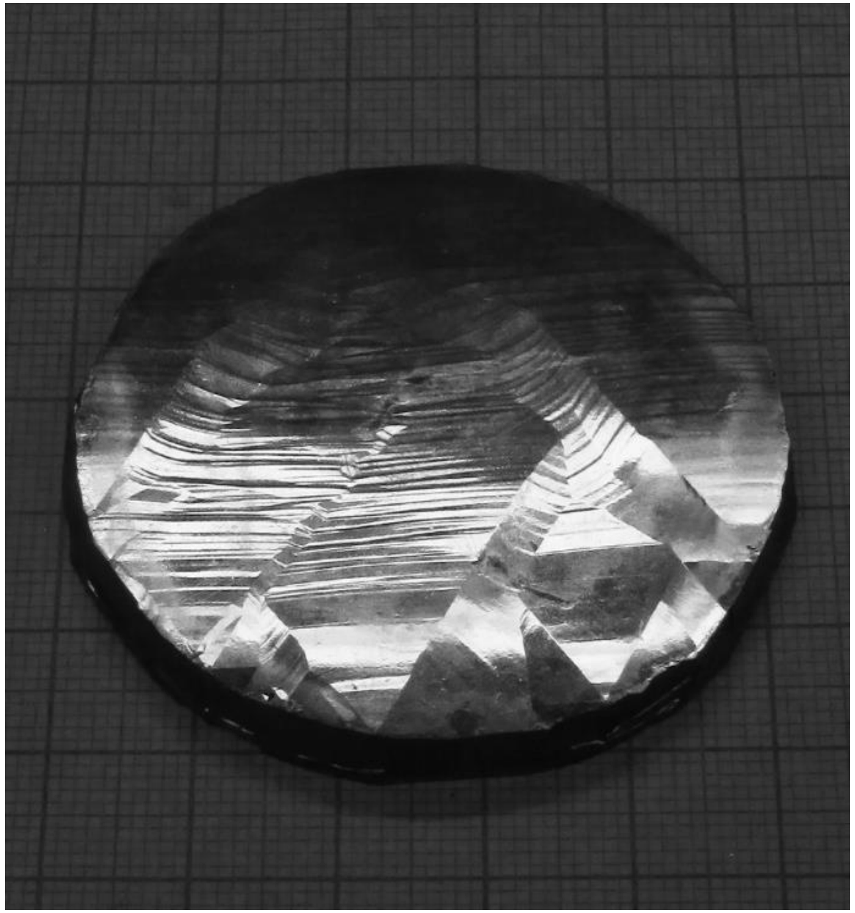


Sample under UV illumination indicates different dopant incorporation within “carrots”

L. Kirste et al., Materials 2021, 14, 5472.

Ammonothermal GaN Crystals – Morphology

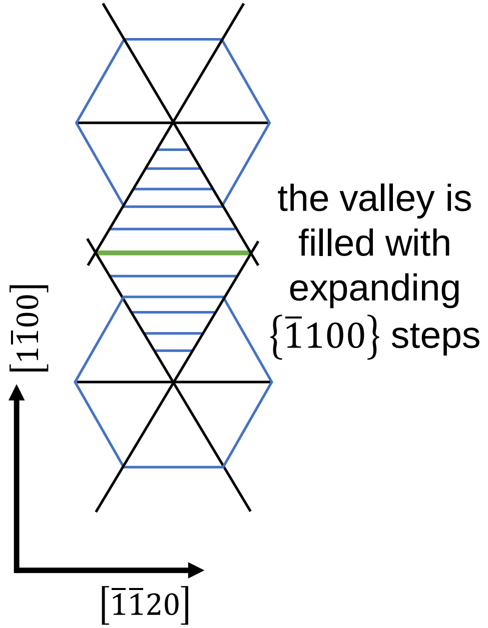




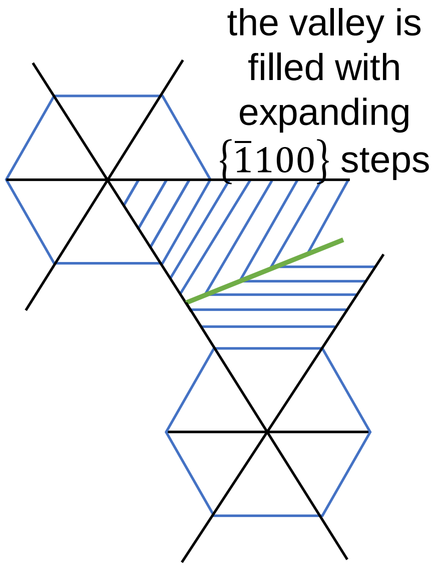
Ammonothermal GaN Substrates – Surface Defects

- There are three different ways of hillock connection:

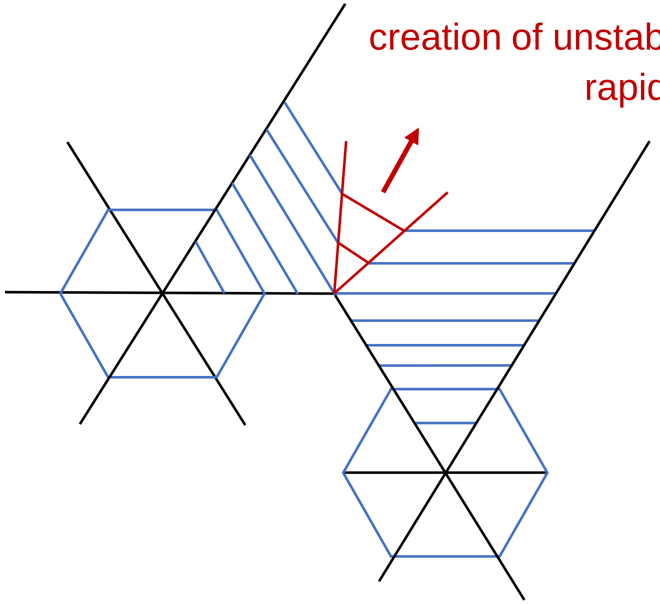
1. Side to side positioned parallel

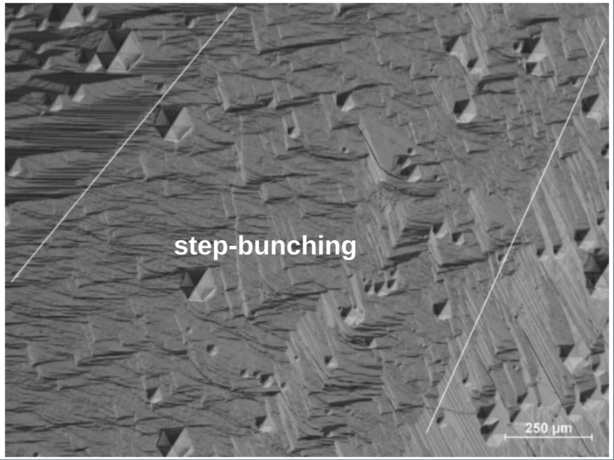


2. Side to side positioned at an angle of 60 degrees



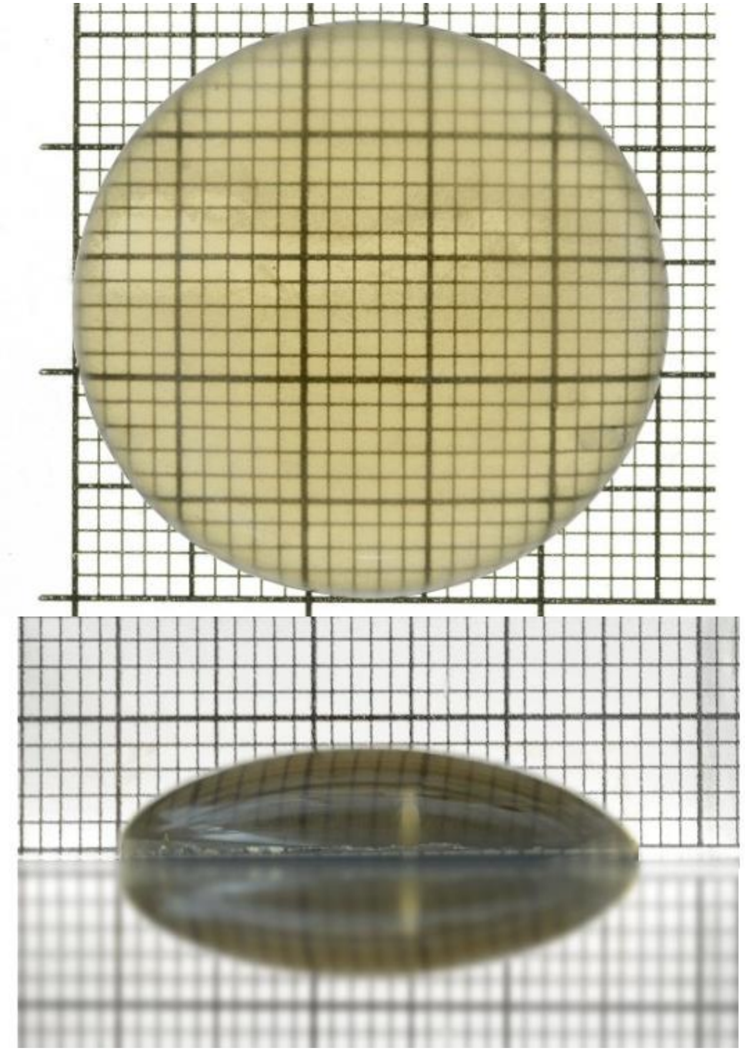
3. Side to side positioned at an angle of 120 degrees



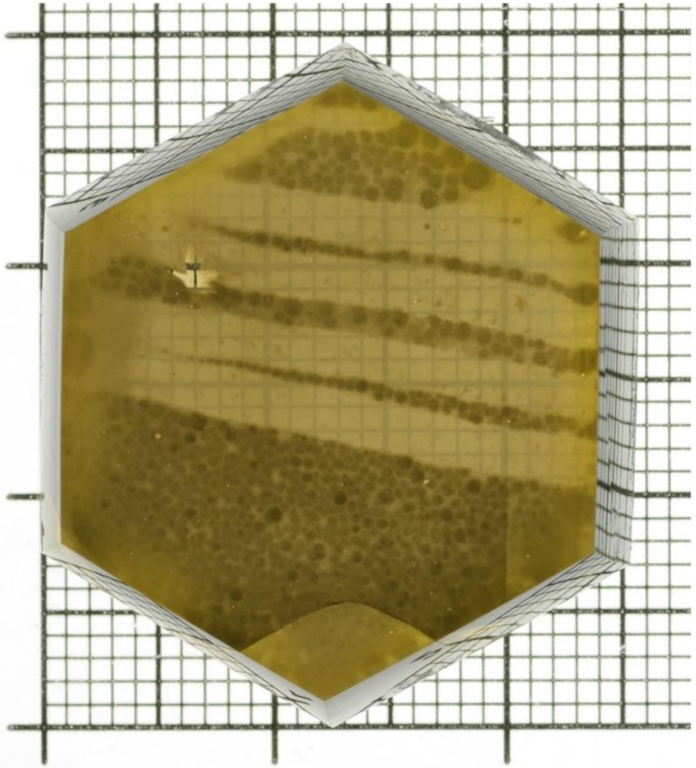


T. Sochacki et al., Materials, 2023 Apr 25;16(9):3360.

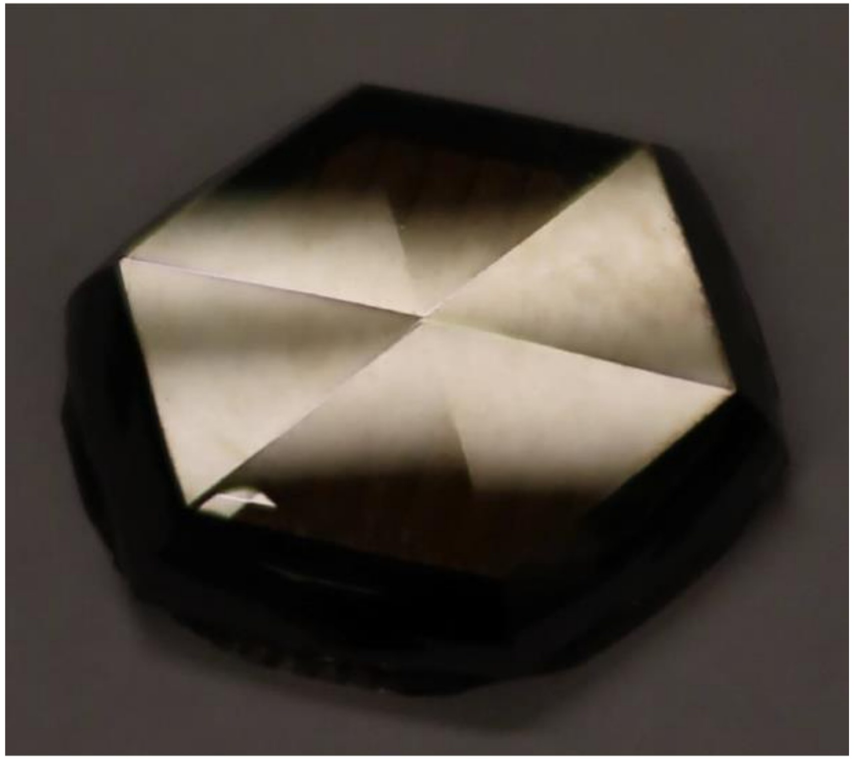
Ammonothermal GaN Crystals – Future Solution



Lens seed

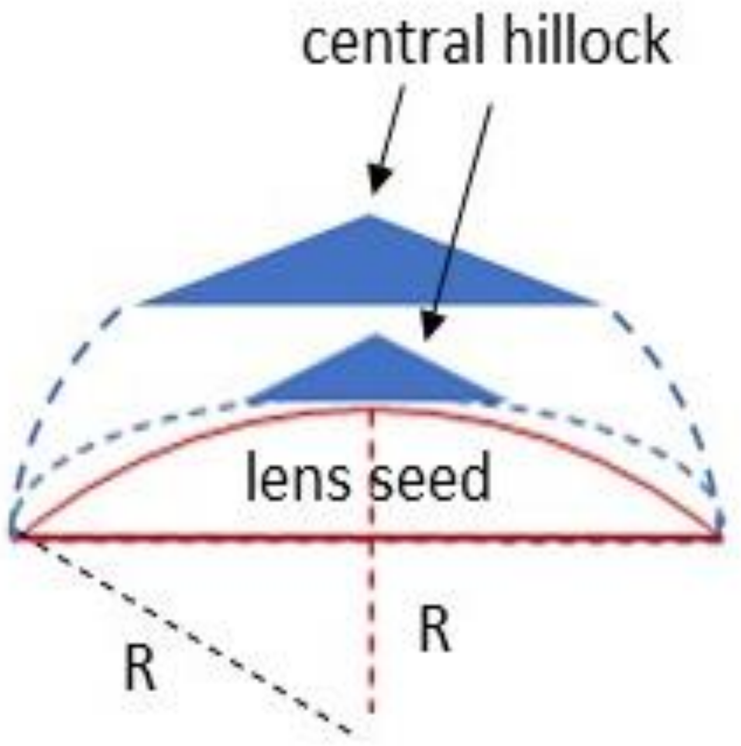


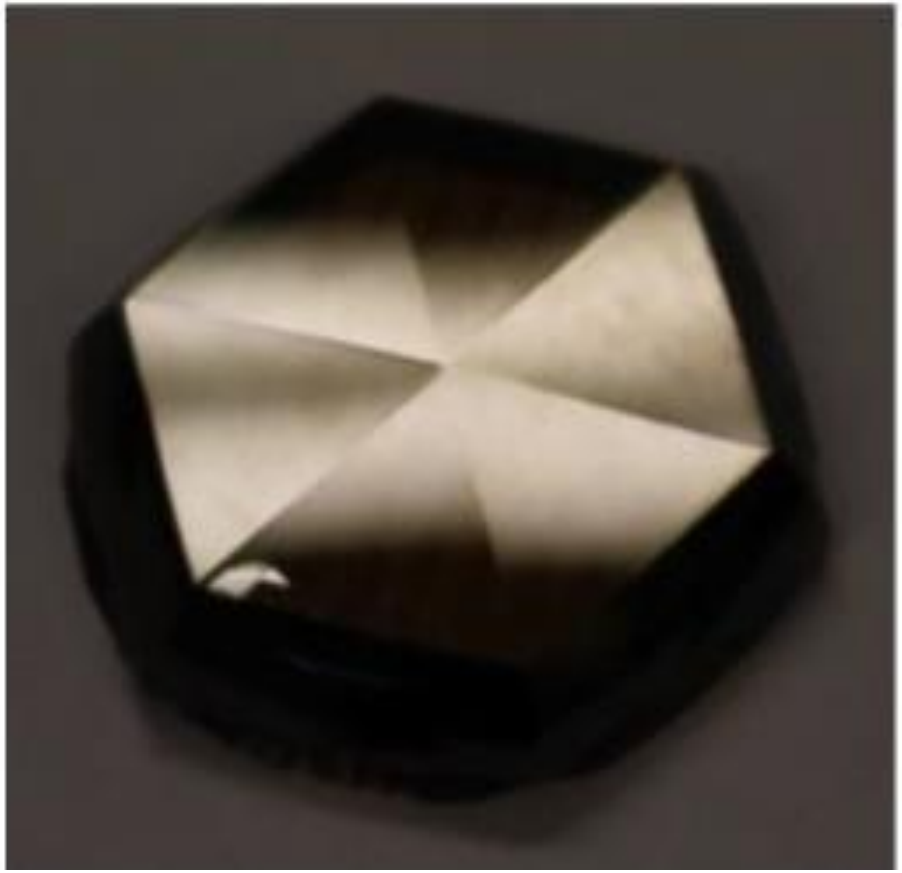
As-grown GaN



One hillock

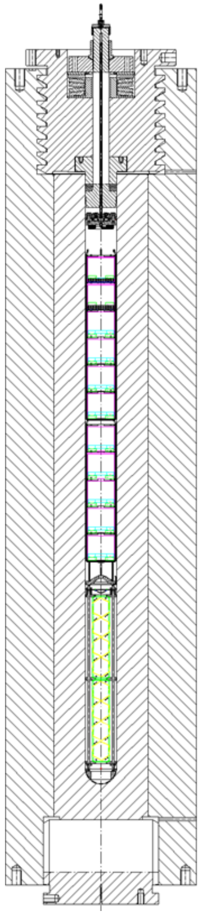
Ammonothermal GaN Crystals – Future Solution





Road Map for 4-inch and 8-inch Crystals&Substrates

Φ_{int} = 100 mm



- Working conditions:

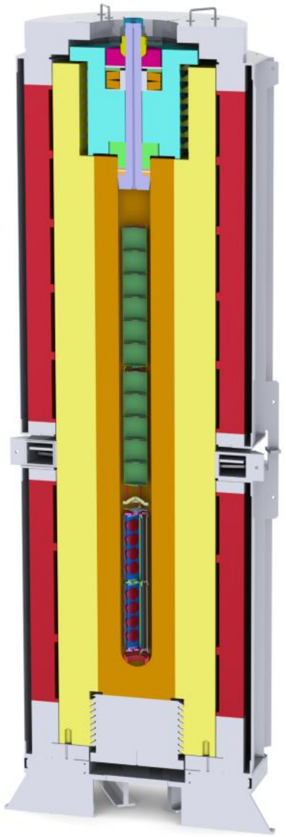
  Maximum working pressure – 400 MPa

  Maximum working temperature – 600˚C

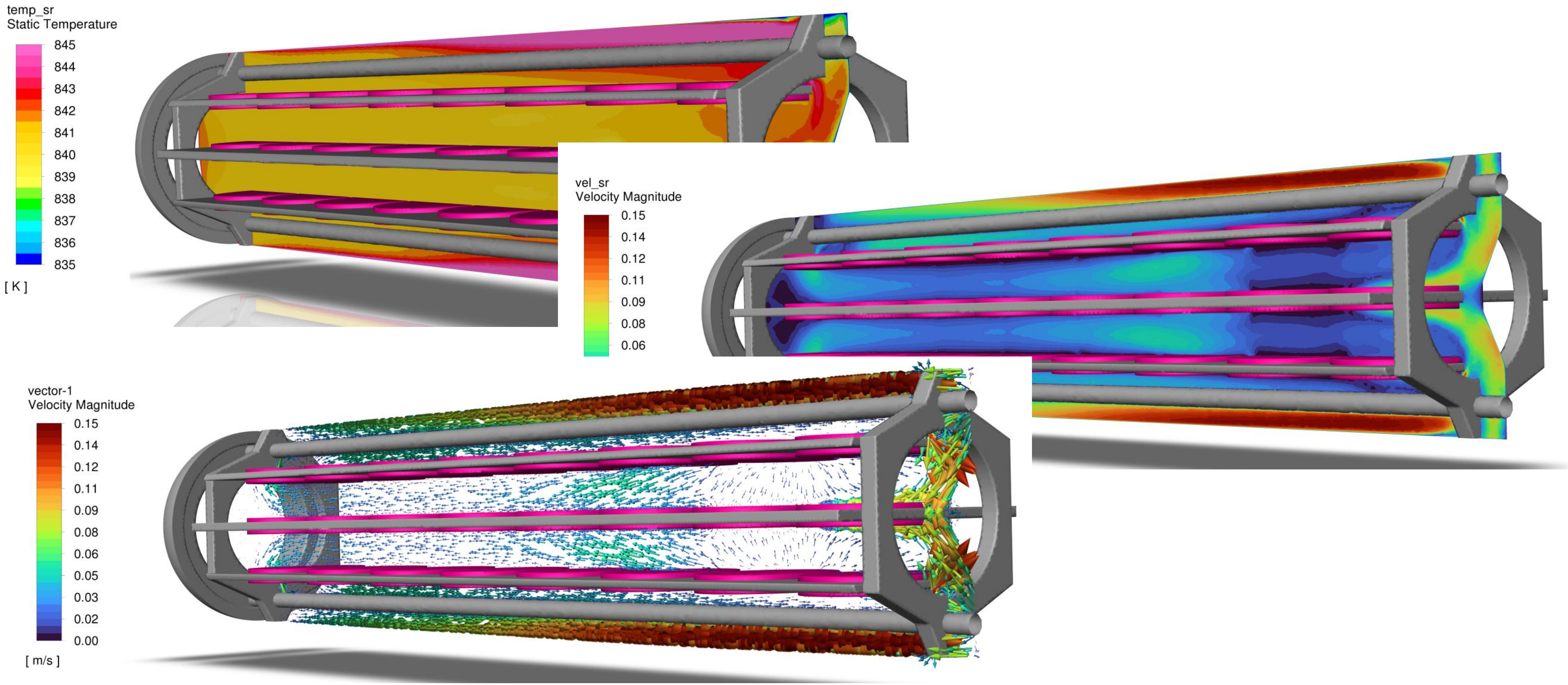
  Crystallization process duration ~ 70 days

- One year to build new autoclaves (2024)
- Three years to grow the first 4-inch seeds (2025-2027)
- One year to demonstrate and sell the first 4-inch substrates (2028)

Φ_{int} = 120-130 mm



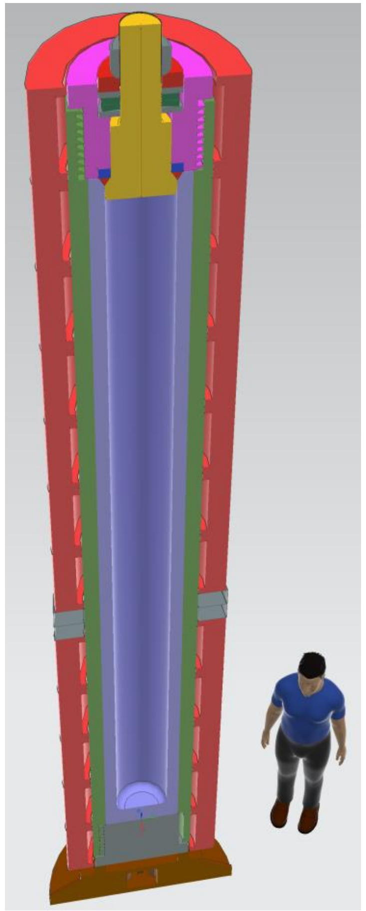
Road Map for 4-inch and 8-inch Crystals&Substrates



M. Zak

Road Map for 4-inch and 8-inch Crystals&Substrates

Φ_{int} = 300 mm



- Working conditions:

  Maximum working pressure – **100 MPa**

  Maximum working temperature – 600˚C → **Different chemistry is needed**

  Crystallization process duration – ~ 150 days

Chemical reactions (simplified):

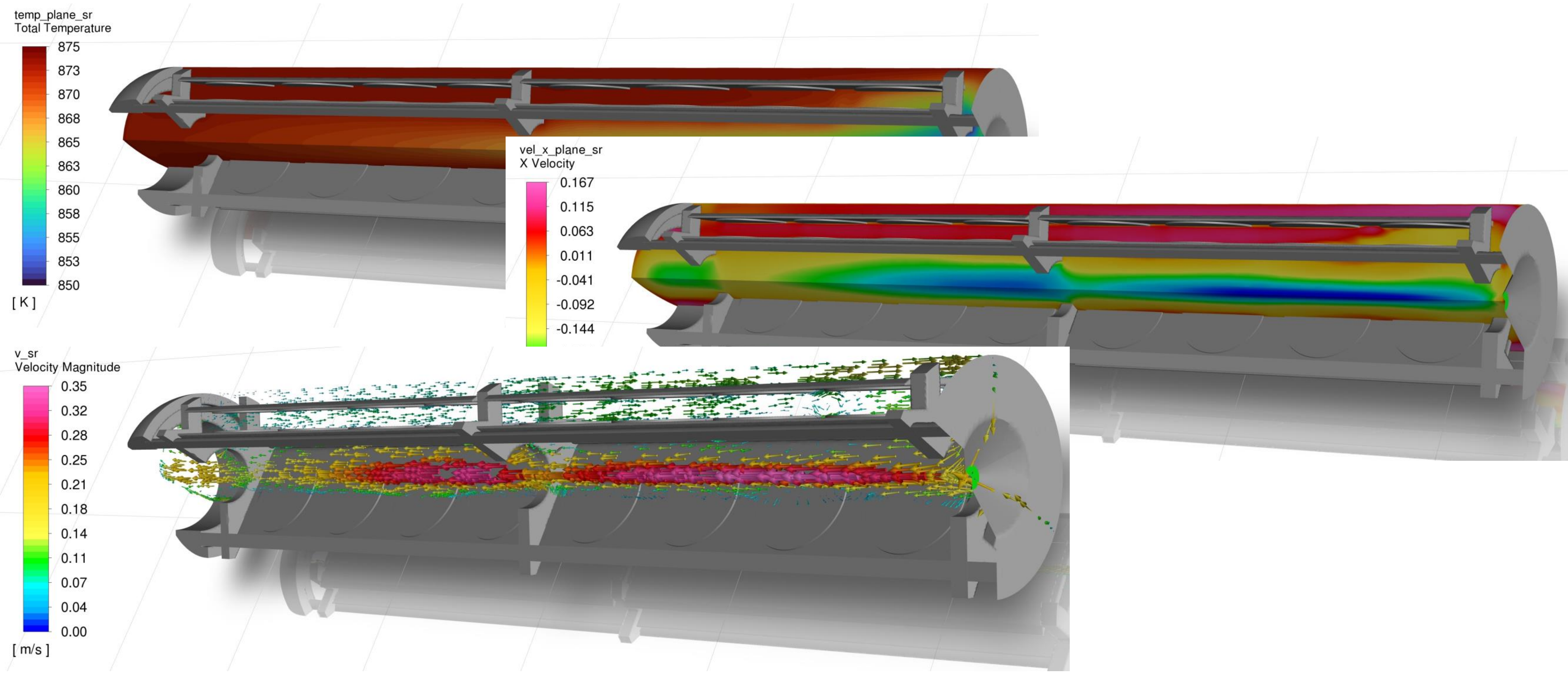
~~$2Na + 2NH_3 \rightarrow 2NaNH_2 + H_2$~~

~~$2Ga + 2NH_3 \rightarrow 2GaN + 3H_2$~~

~~$2NaNH_2 + GaN + 2NH_3 \leftrightarrow Na_2Ga(NH_2)_5$~~

- Two years to create new technology (2024-2026)
- One year to build a new autoclave (2027)
- Four years to grow the first 8-inch seeds (2026-2030)
- **First 8-inch crystals and substrates in 2030**

Road Map for 4-inch and 8-inch Crystals&Substrates



M. Zak

Summary

- **Two-inch ammonothermal GaN substrates** of the highest structural, optical and electrical quality are fabricated and **available on the market.**
- Details of basic ammonothermal growth method were demonstrated.
- Defects in crystals were shown and discussed.
- Road map for **4-inch** and **8-inch** ammonothermal GaN substrates was presented
    - Four-inch ammonothermal GaN substrates in **2028**
    - Eight-inch ammonothermal GaN substrates in **2030.**

Acknowledgement

Polish National Science Centre (NCN) through OPUS projects: 2018/29/B/ST5/00338, 2020/37/B/ST5/03746, 2021/41/N/ST5/03669 and 2021/41/N/ST5/04518

Polish National Centre for Research and Development through project TECHMATSTRATEG-III/0003/2019-00

GaN4AP project, which has received funding from the ECSEL Joint Undertaking (JU) under grant agreement No 101007310. The JU receives support from the European Union's Horizon 2020 research and innovation programme, and Italy, Germany, France, Poland, Czech Republic, Netherlands.

ONR Global through NICOP project N00014-21-S-B001; GRANT13353748.

unipress

Thank you for your attention