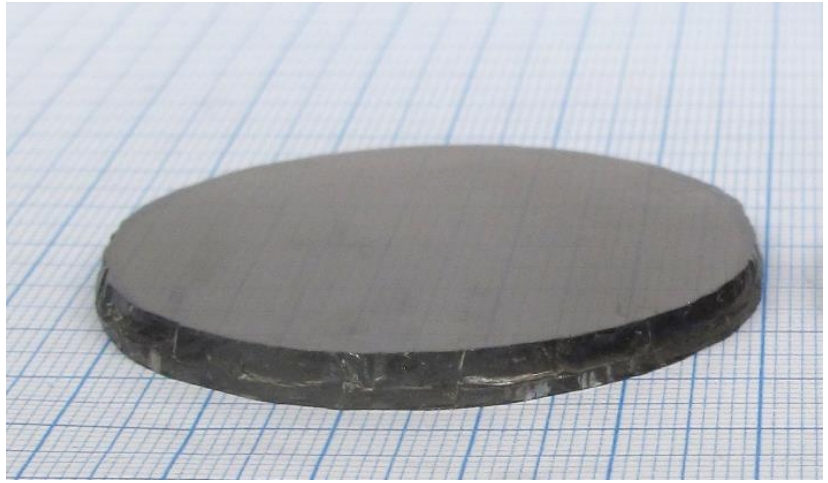
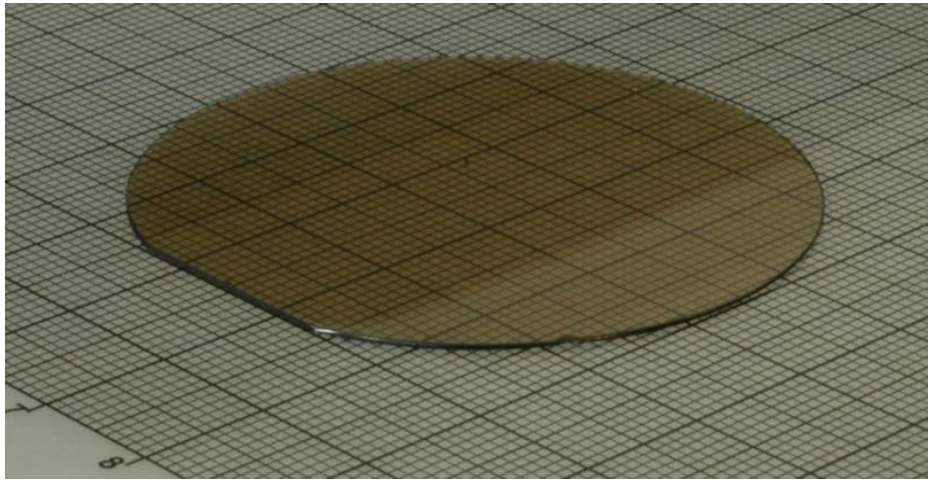
Recent progress in basic ammonothermal growth of gallium nitride

From crystal to substrates



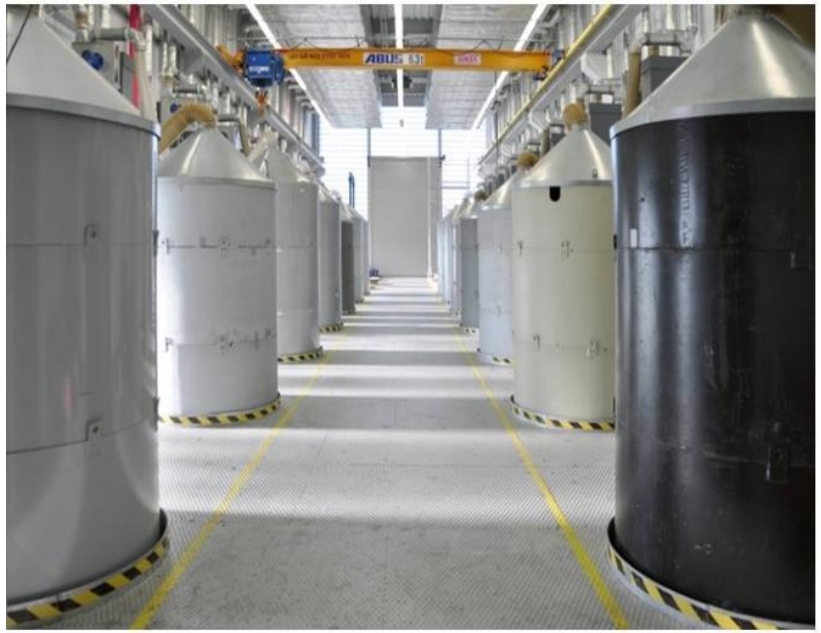
As grown crystals

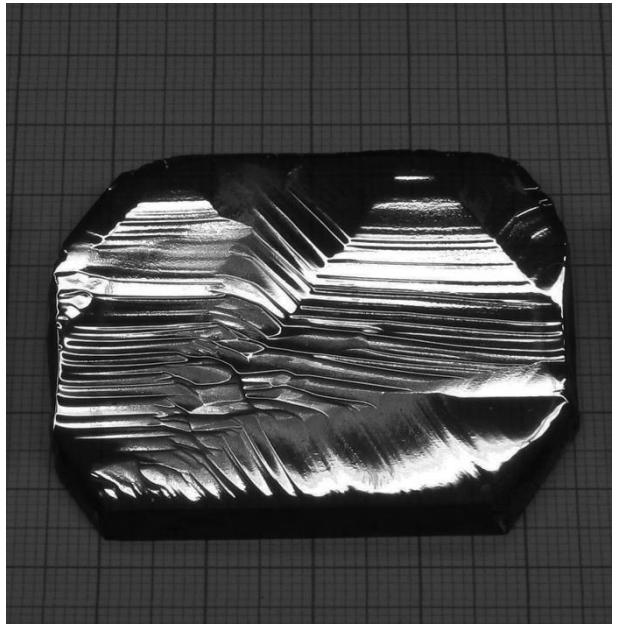


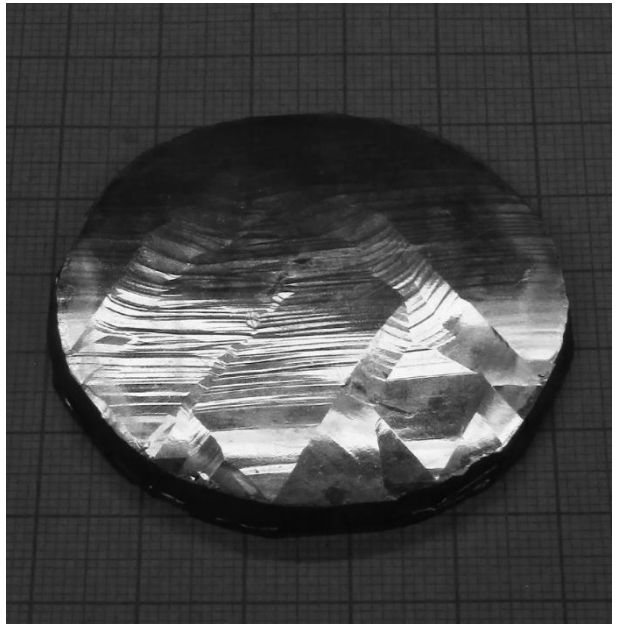
Substrate

Basic ammonothermal method

- analog to hydrothermal crystallization of quartz,
- **ammonia in a supercritical state** (enhanced reactivity),
- applied pressure and temperature: **300-400 MPa and 450–600^{o}C,**
- **mineralizers (alkali metals)** - increased solubility of GaN feedstock.



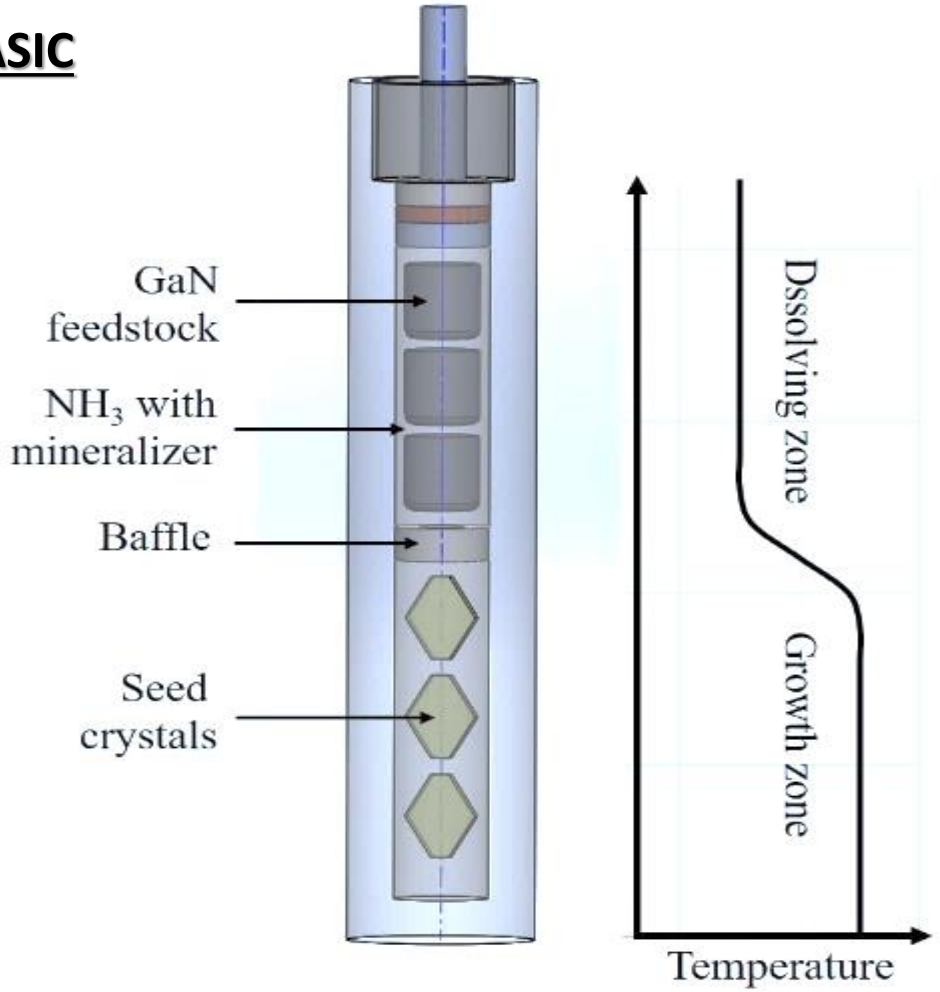




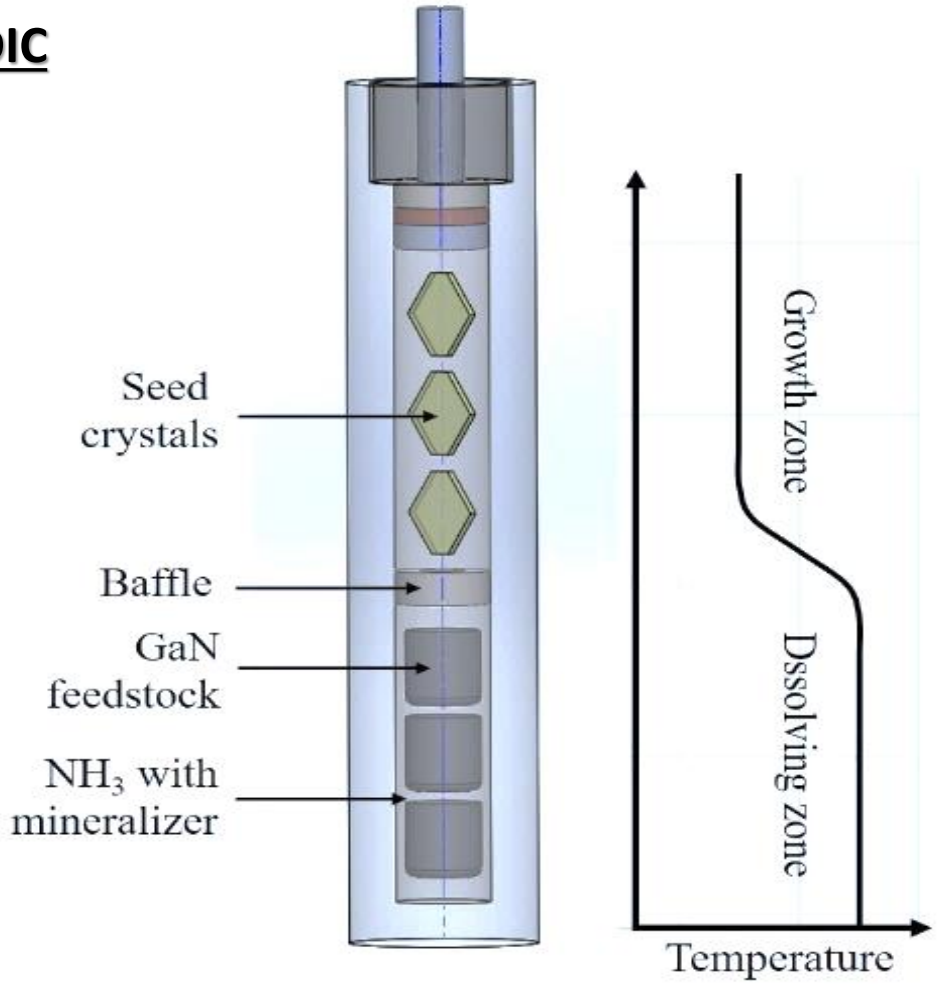
R. Dwilinski et al., J. Cryst. Growth 310 (2008) 3911.

Ammonothermal method

BASIC

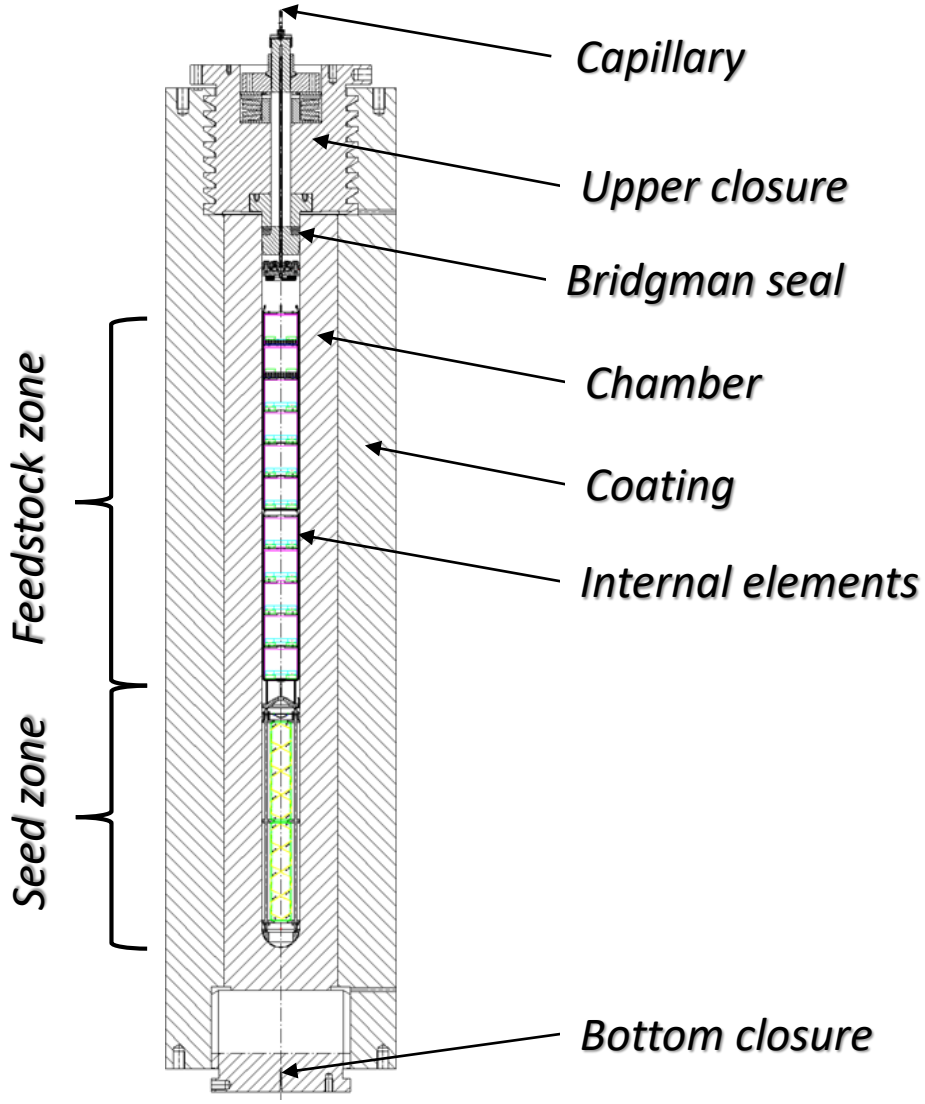


ACIDIC

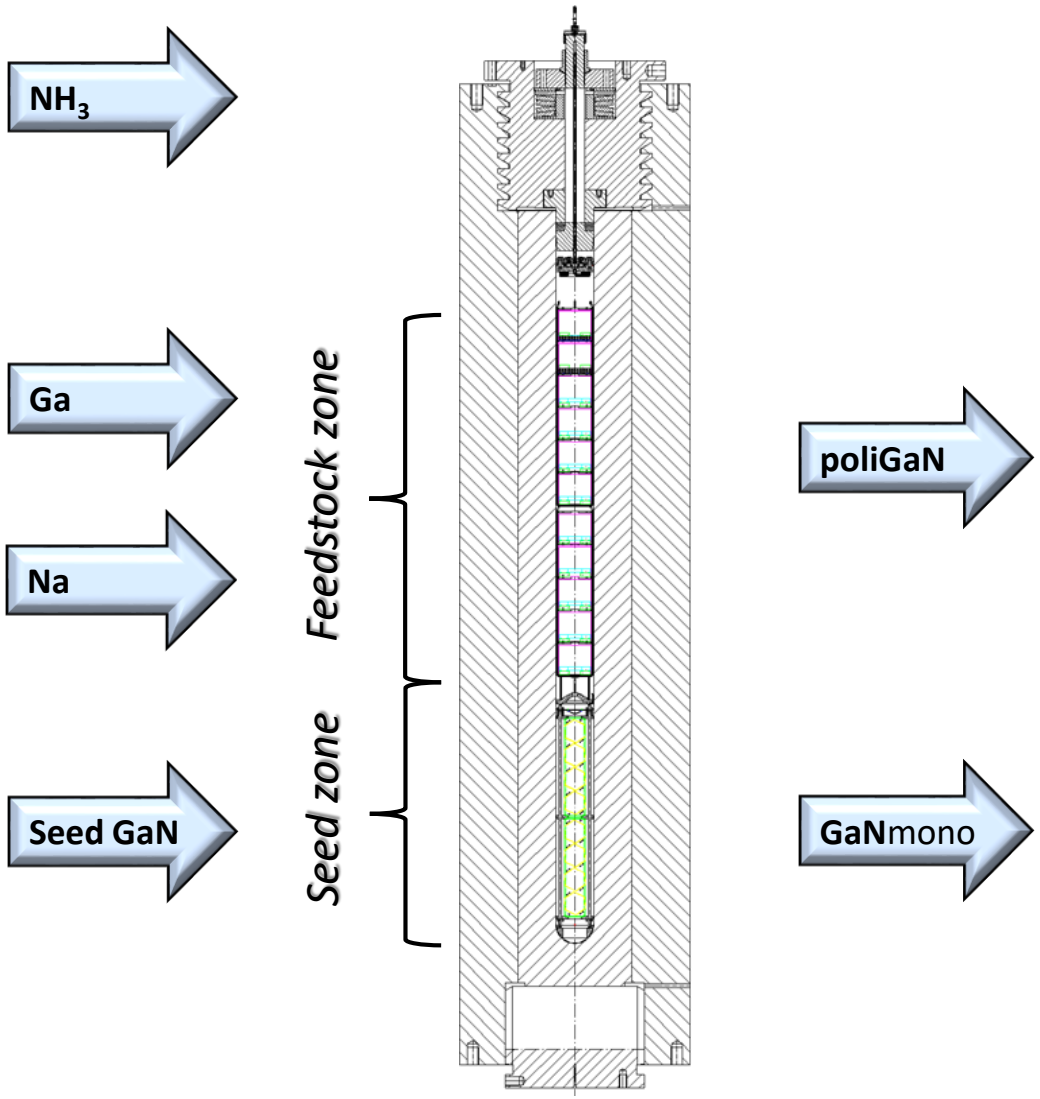


Mineralizers: Alkali metals Halide compounds

Scheme of autoclave



Scheme of autoclave



Working conditions:

- Maximum working pressure – **3.7 kbar**
- Maximum working temperature – **600˚C**
- Recrystallization process duration ~ **70 days**

Chemical reactions (simplified):

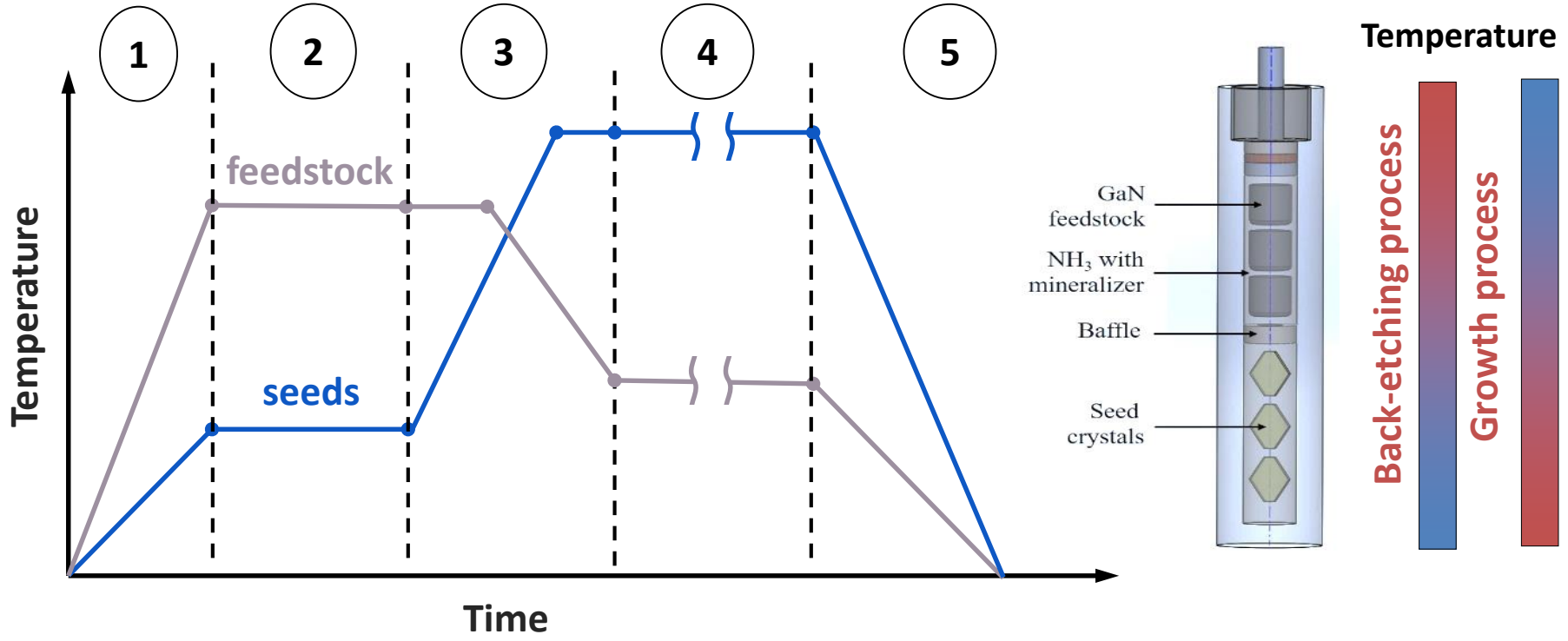
$Ga + NH_3 \rightarrow GaN + {}^3/_2H_2$

$Na + NH_3 \rightarrow NaNH_2 + {}^1/_2H_2$

Conversion of Ga → $GaN_{monocrystal}$ – **80%**

Basic ammonothermal method – process stages

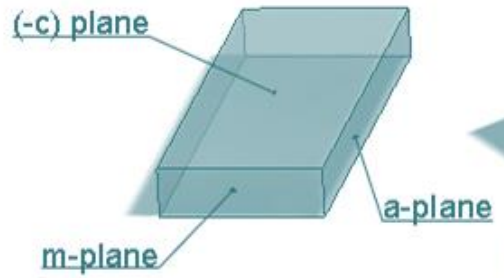
1. Heat-up
2. **Back-etching** of the seeds at lower temperature - coupling of the solution with seeds
3. **Temperature transition**
4. **Growth** at higher temperature/dissolution of the feedstock at lower temperature
5. Cool-down



Basic ammonothermal method – growth stages

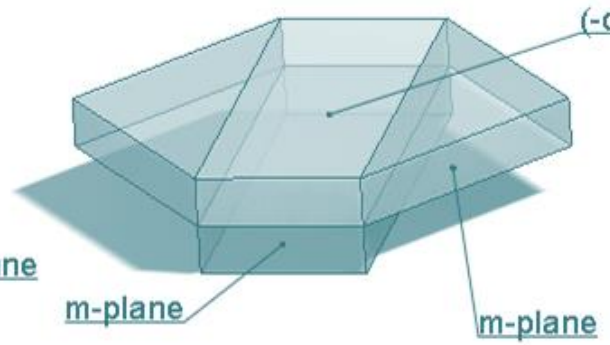
Stage 1

Growth of seed



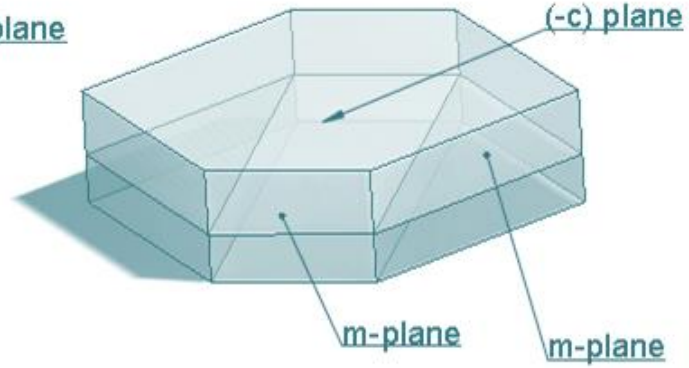
Stage 2

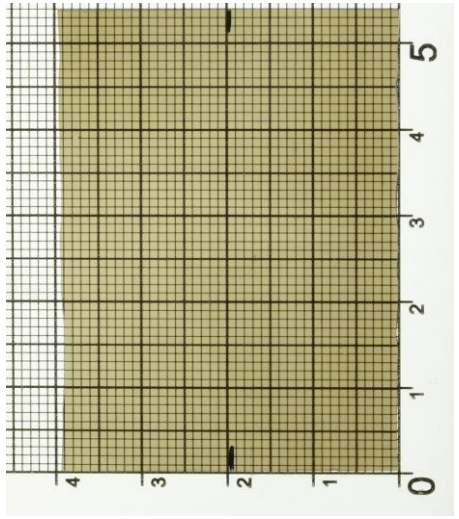
Lateral growth

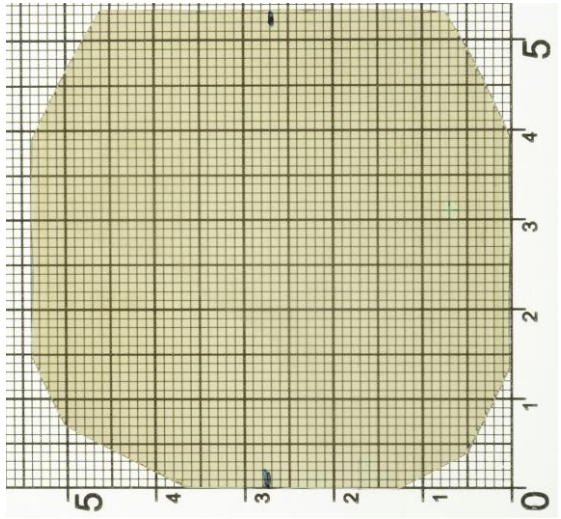


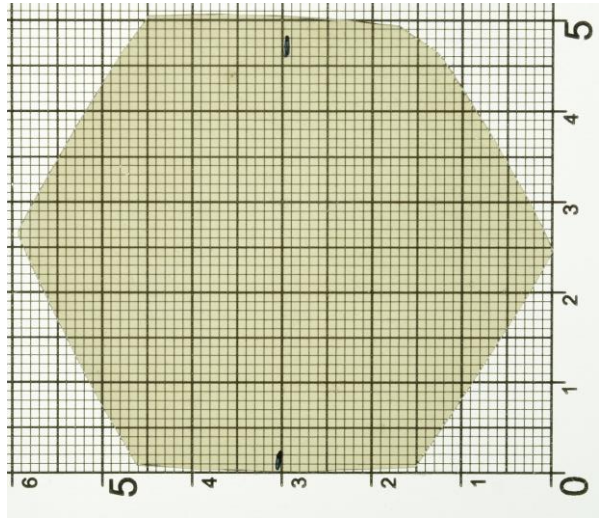
Stage 3

Crystal multiplication





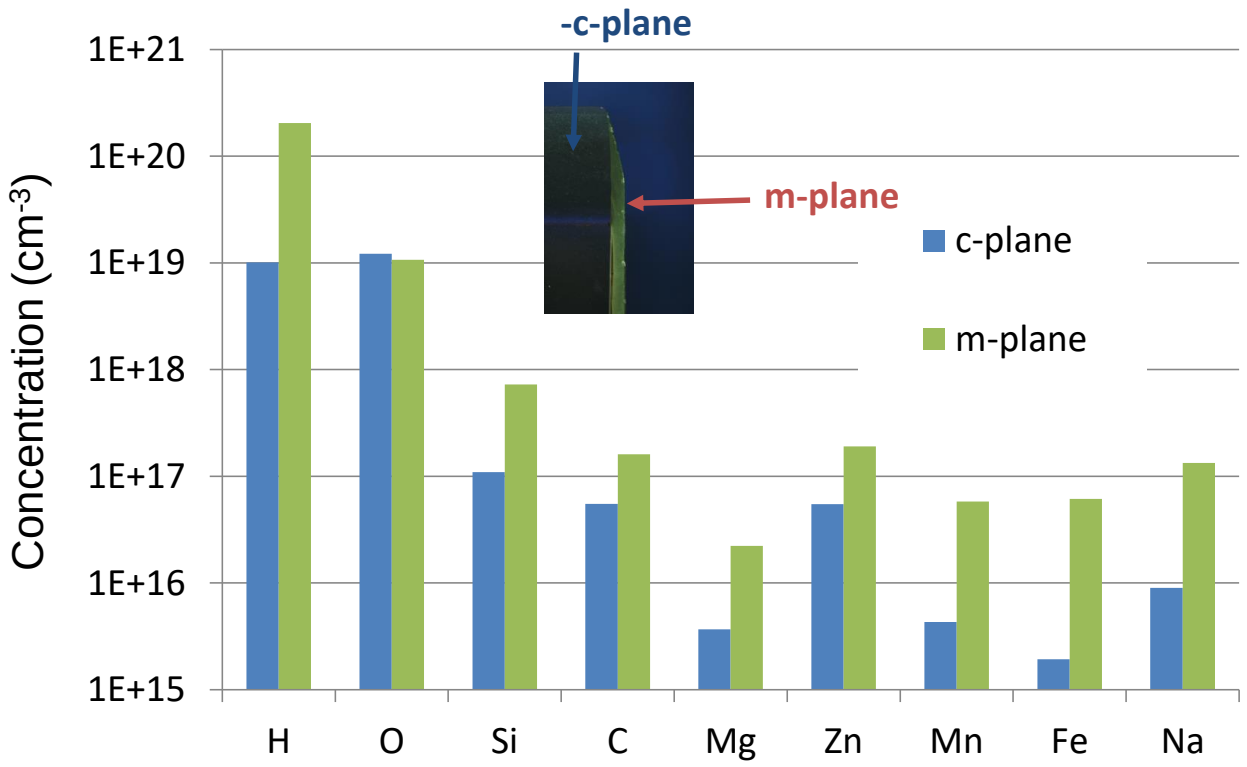


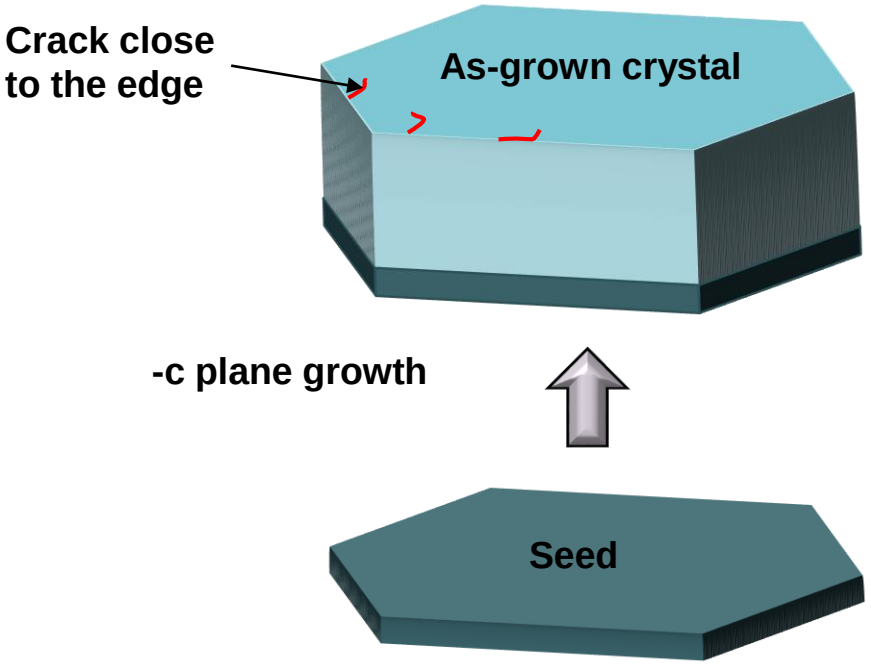


[10-10]

[11-20]

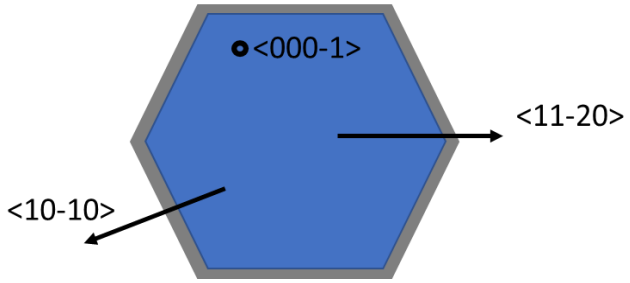
Ammonothermal GaN – limiting factor

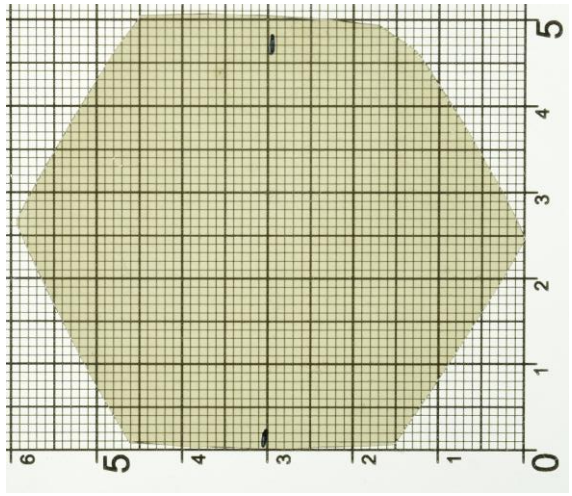


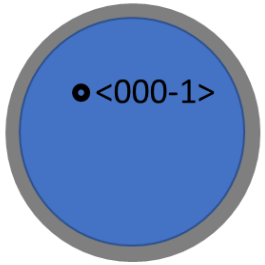


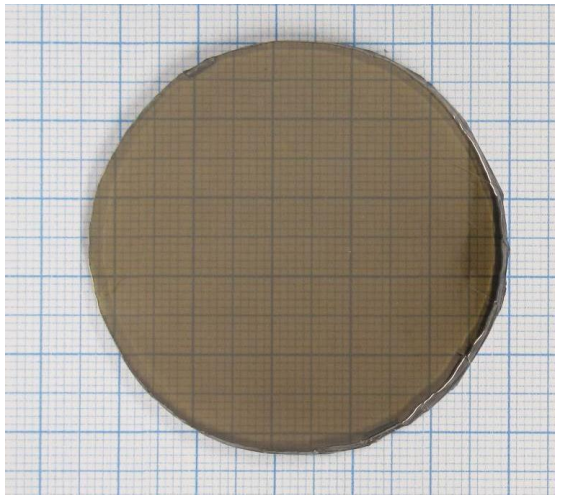
M. Zajac et al., Progress in Crystal Growth and Characterization of Materials 64 (2018) 63–74.

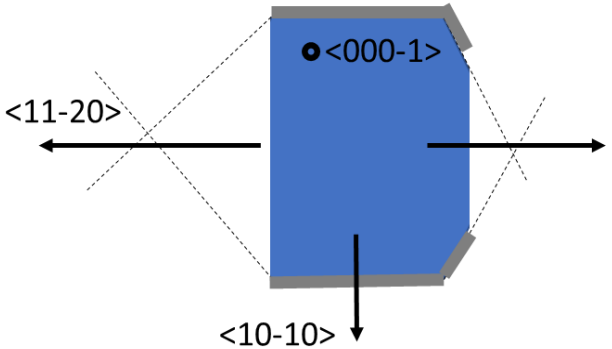
Different shapes of seeds

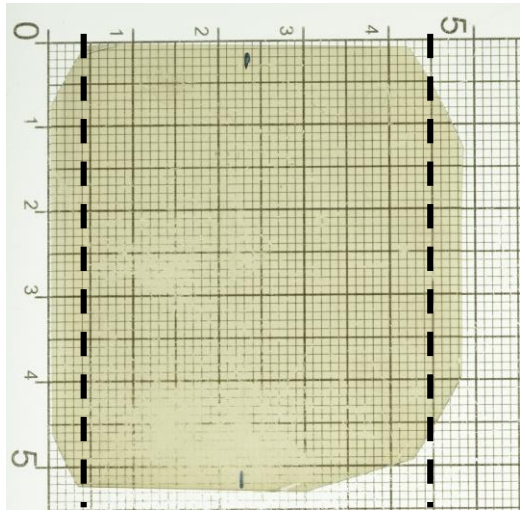


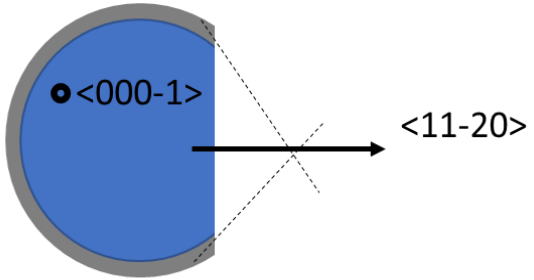


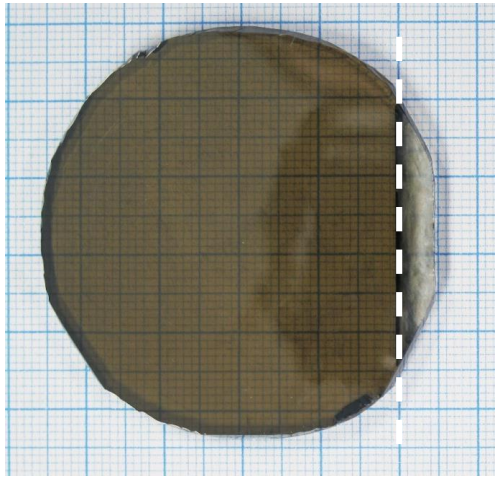










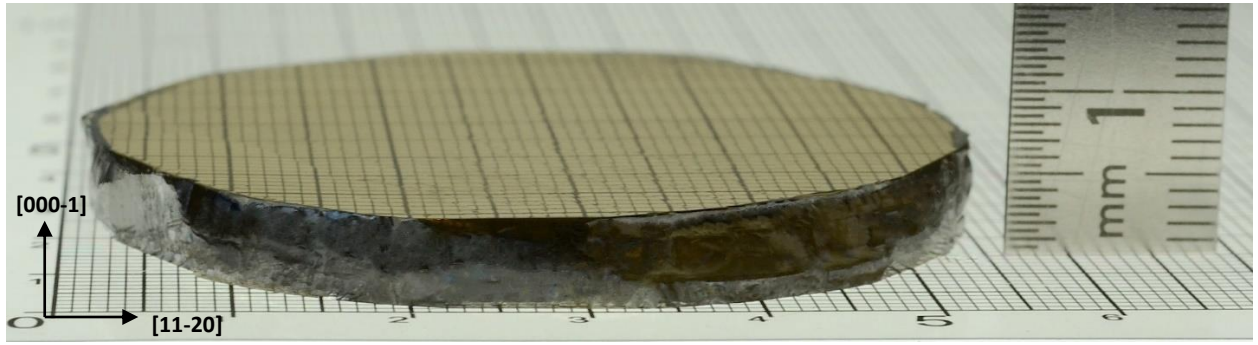


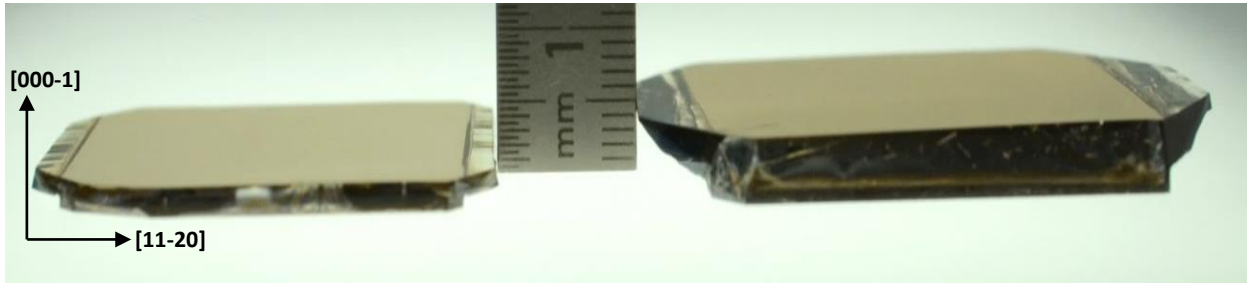
Different shape of seeds and blocking growth in lateral direction by metal borders

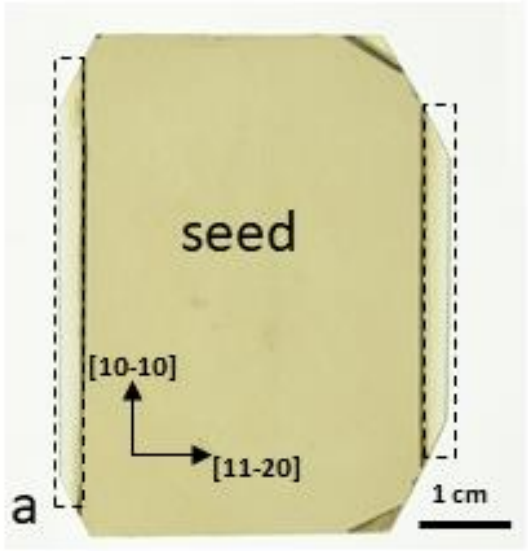
Bulk GaN crystals – one growth run

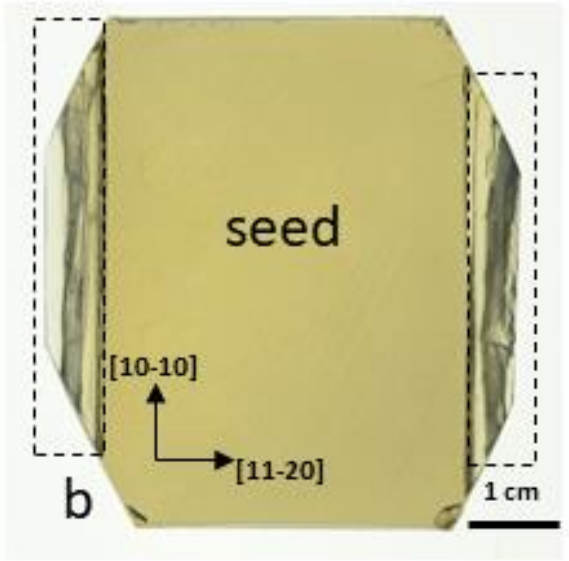
- Growth in [000-1] direction ~3 months
- Increased supersaturation
- Increased growth rate from 23 µm/day to 60 µm/day

- **Vertical expansion** (in one run)**: 4mm** (previously 2mm)
- **Lateral expansion** (in one run)**: 7mm** (previously 4mm)



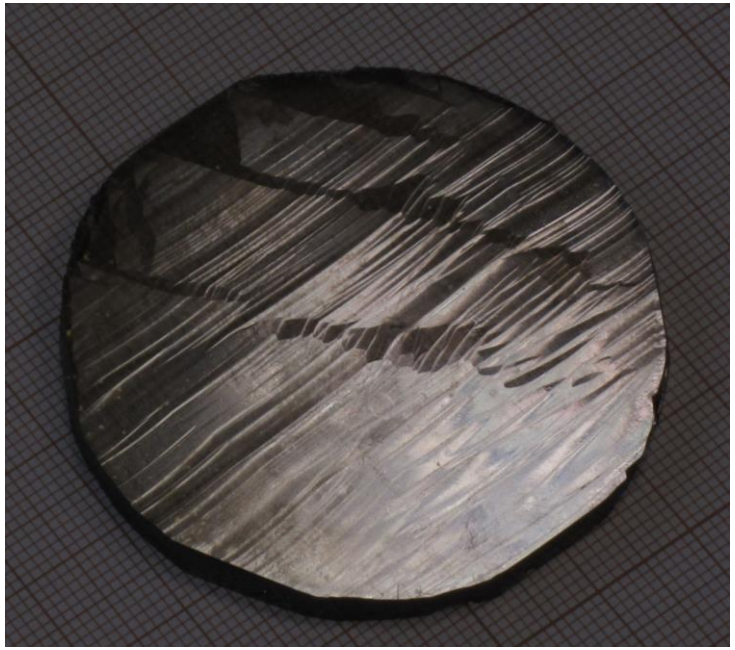




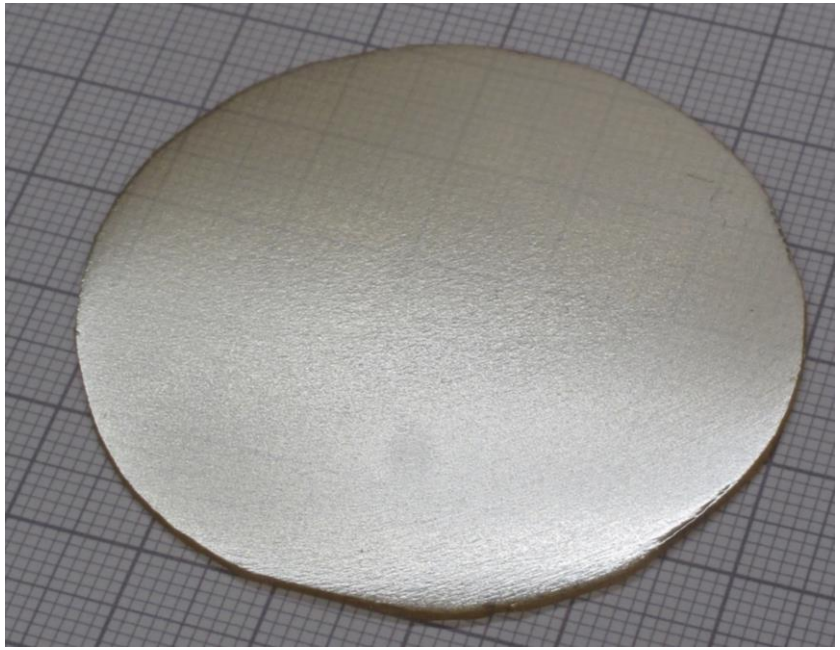


Preparation of seeds

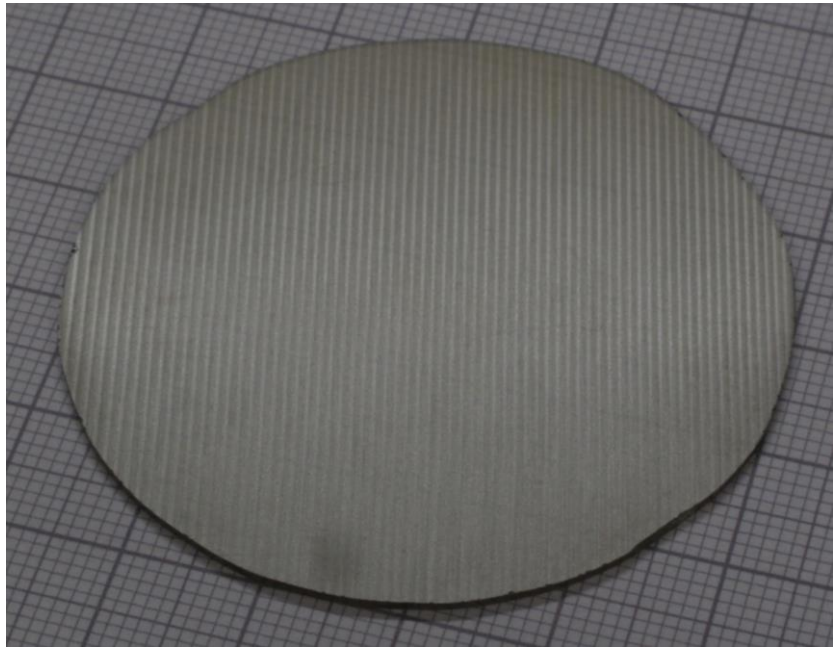
After growth



After grinding

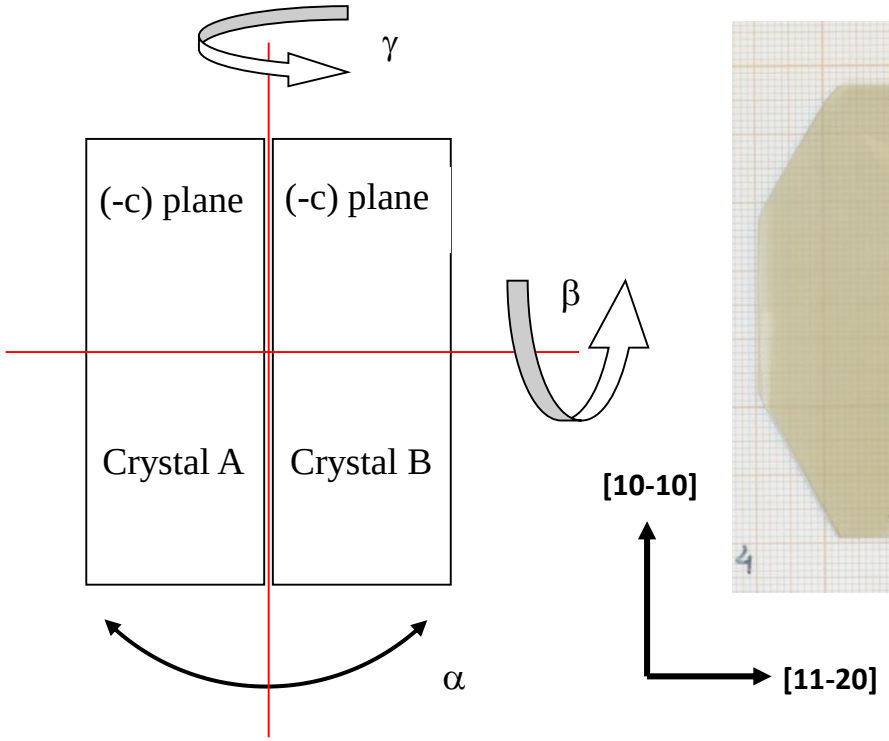


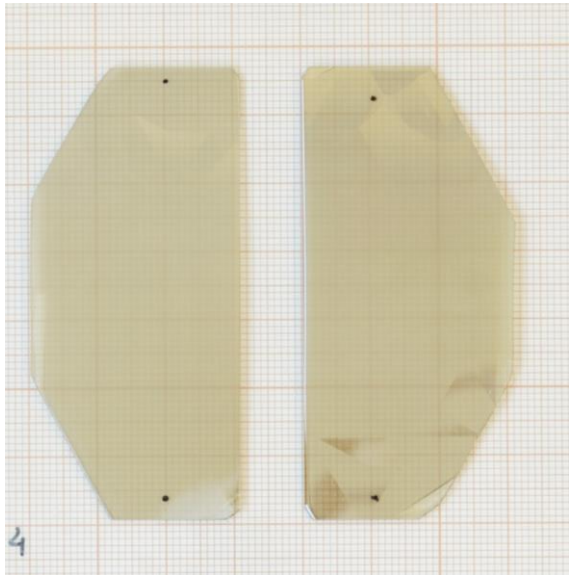
After slicing

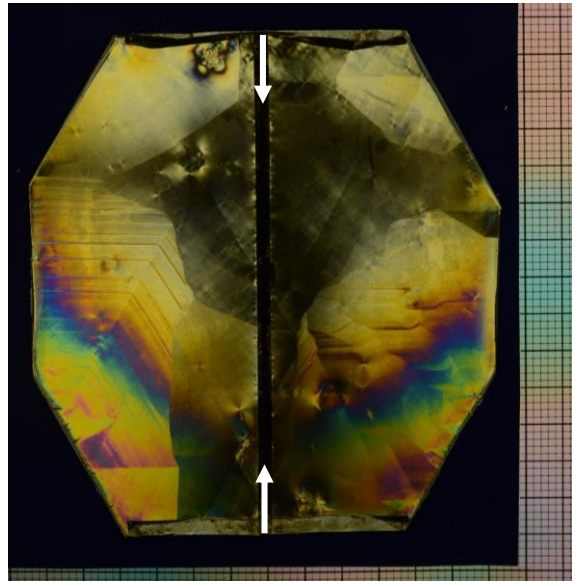


Tiling technology

Road to 2 inches or more

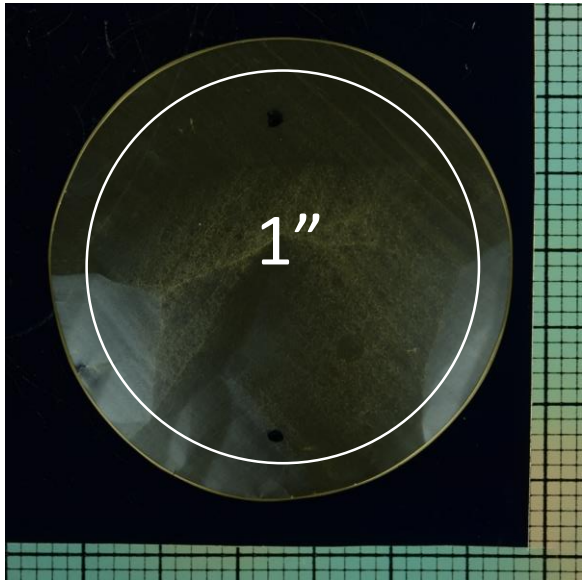


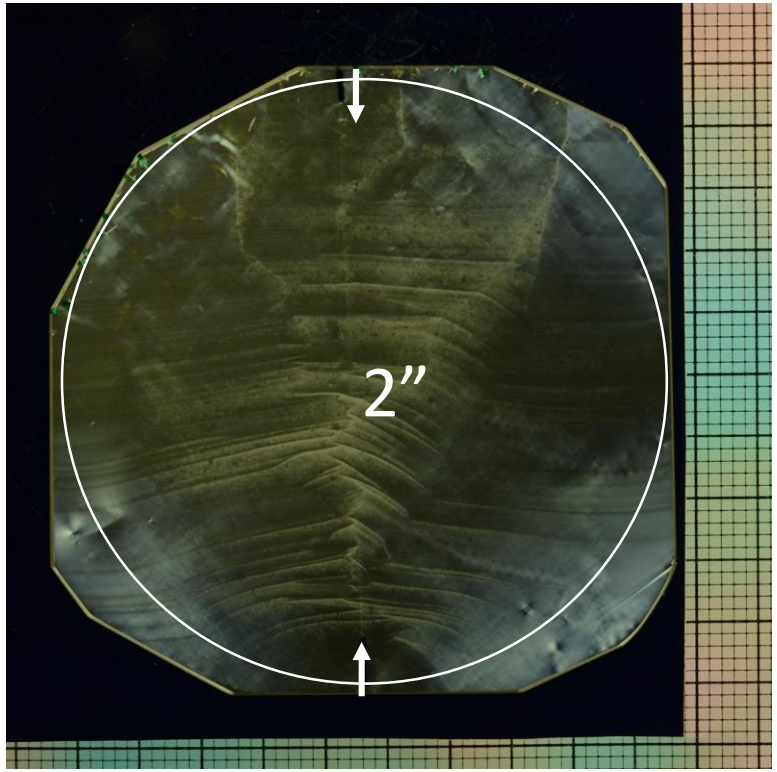


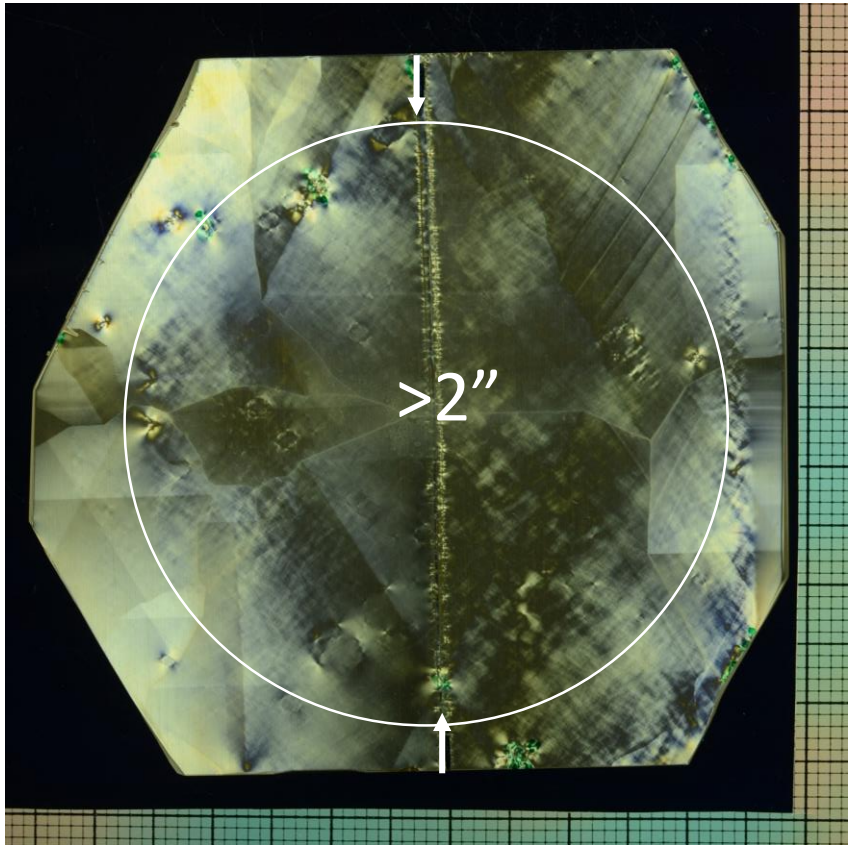


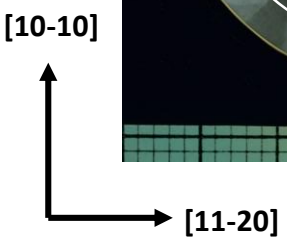
Misorientation (˚)	max (α, β, γ) ≤ 0.03˚

Tiling technology - examples

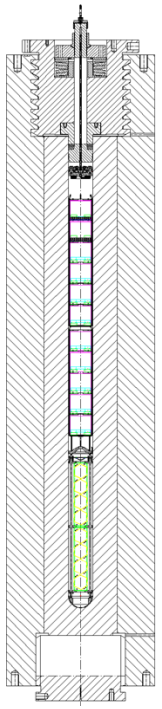




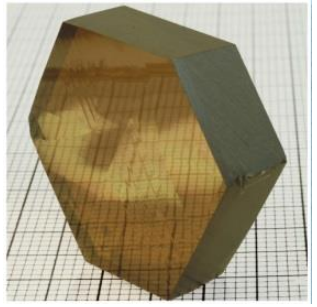


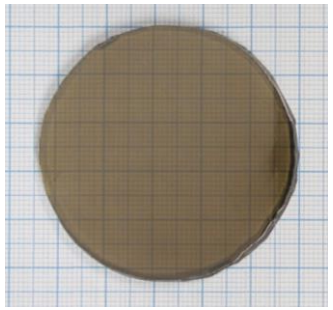


Production of substrates

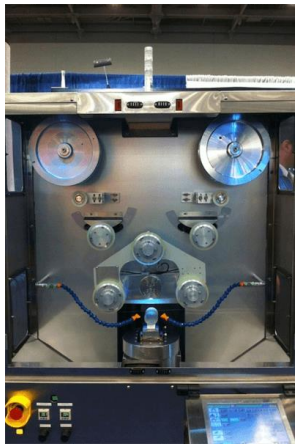


Recrystallization

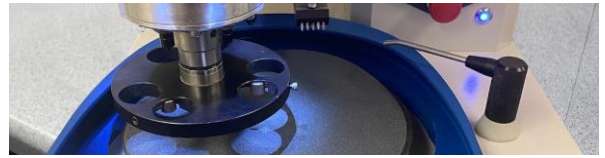




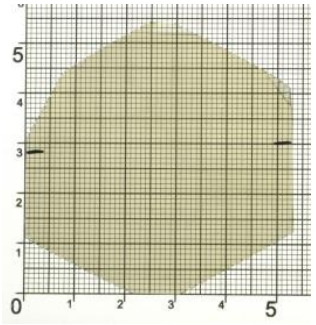
As-grown crystals

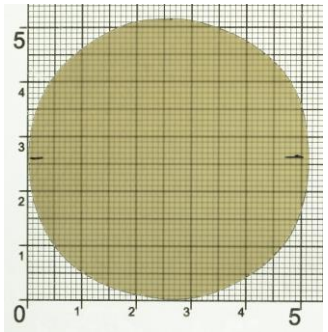


Machining process

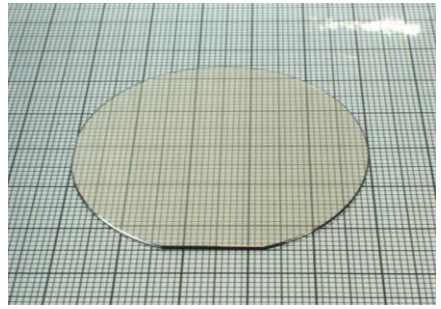


Seeds





Substrates



From crystal to substrates – wafering

PRODUCT DATA SHEET **Cn0050-241-002-5-2-n100**

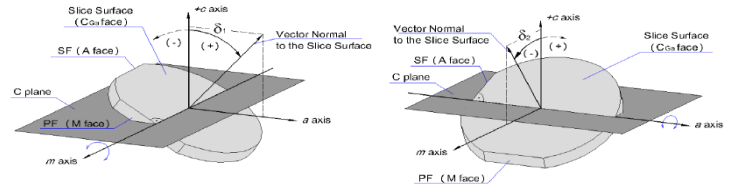
2 inch C-plane n-type high-electron-concentration AMMONO-GaN substrate, oxygen-doped.
The substrate is sliced from a mono-crystalline bulk material grown by ammonothermal method.

TECHNICAL SPECIFICATION

DESCRIPTION		UNIT	VALUE
General specification			
	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
Structural specification			
	Etch Pit Density (EPD)	cm^{-2}	< 5×10^4
	FWHM (0002) of X-ray rocking curve, epi-ready surface at 100 µm x 100 µm slit	arcsec	~ 20
	Macro defects		none
Electrical specification			
	Type of conductivity		n type
	Carrier concentration	cm^{-3}	~ 10^{19}
	Resistivity	Ω*cm	~ 10^{-3}
	Carrier mobility	$cm^2/V*s$	~ 150

MISORIENTATION

(measured in the center of the substrate)



Off M face		deg	0 (±0,25)
C face	angle δ_1	deg	0 (±0,20)
	angle δ_2	deg	±0,3 (±0,20)

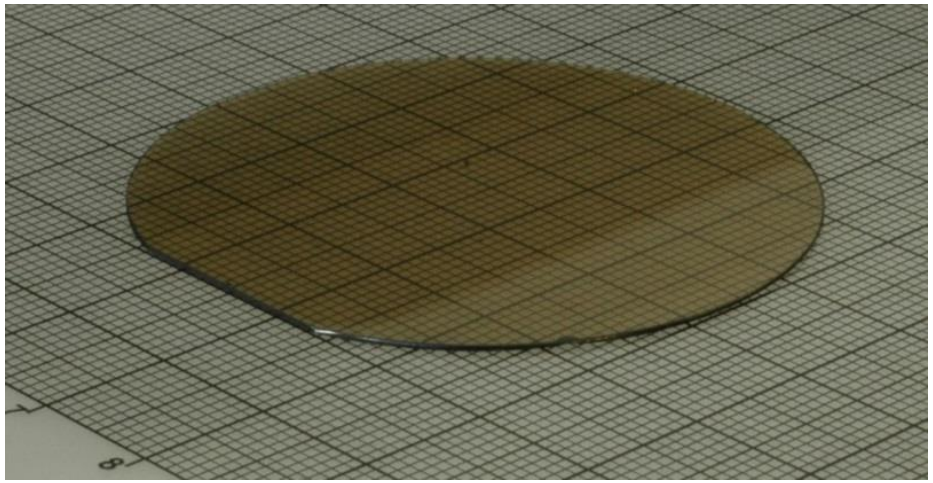
SURFACE PREPARATION

Front side			Epi-ready polished (RMS < 0,5 nm)
Back side			Ground

SUBSTRATE SHAPE

Note: The information given above may be subject to change at any time without notice. This leaflet is not an offer within the meaning of sales or commercial law. The AMMONO-GaN substrates are offered for sale under Ammono's General Terms and Conditions.

www.ammono.com e-mail: sales@ammono.com tel: +48-22-814-0207



Substrate

Wafering stages – orientation of the plane

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

MISORIENTATION

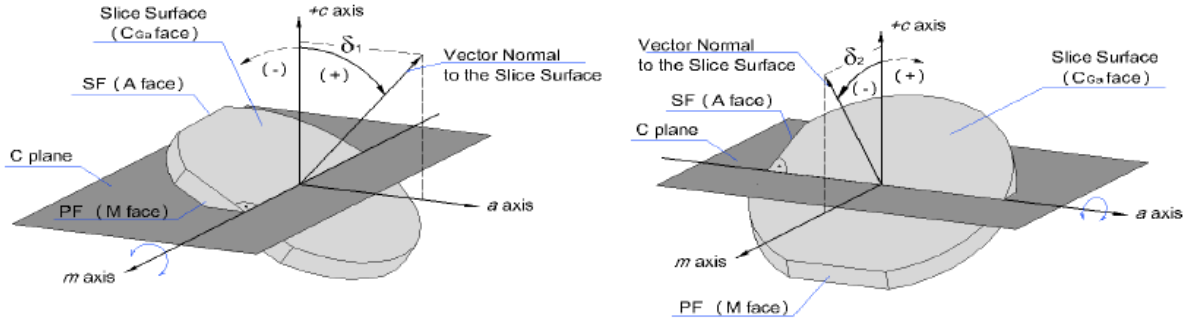
Off M face		deg	0 (±0,25)
C face	angle δ_1	deg	0 (±0,20)
	angle δ_2	deg	±0,3 (±0,20)

SURFACE PREPARATION

Front side			Epi-ready polished (RMS < 0,5 nm)
Back side			Ground

MISORIENTATION

'measured in the center of the substrate)



Wafering stages – slicing

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

MISORIENTATION

Off M face		deg	0 (±0,25)
C face	angle δ_1	deg	0 (±0,20)
	angle δ_2	deg	±0,3 (±0,20)

SURFACE PREPARATION

Front side			Epi-ready polished (RMS < 0,5 nm)
Back side			Ground

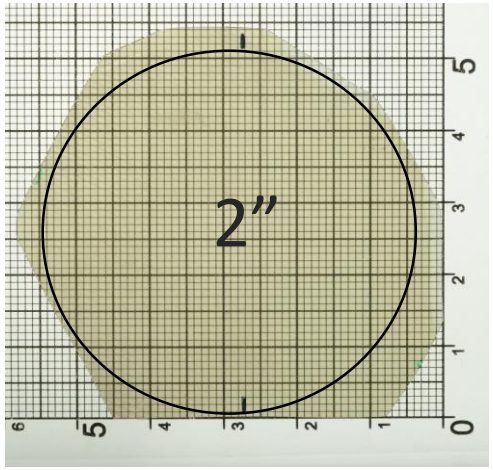
Wafering stages – excision of the substrate

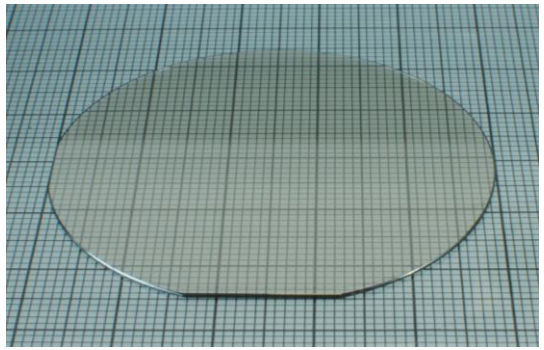
General specification

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

MISORIENTATION

Off M face		deg	0 (±0,25)
C face	angle δ_1	deg	0 (±0,20)
	angle δ_2	deg	±0,3 (±0,20)





SURFACE PREPARATION

Front side			Epi-ready polished (RMS < 0,5 nm)
Back side			Ground

Wafering stages – polishing

General specification

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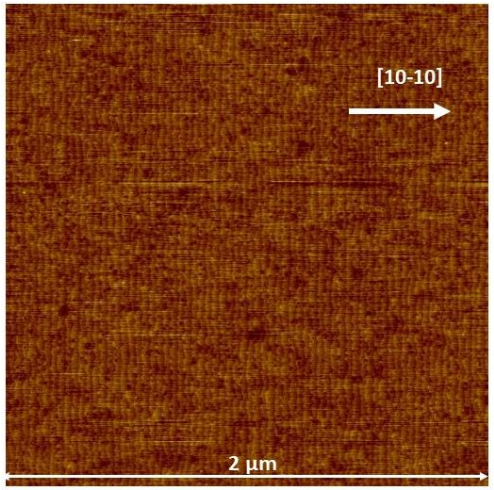
	angle δ_2	deg	±0,3 (±0,20)

SURFACE PREPARATION

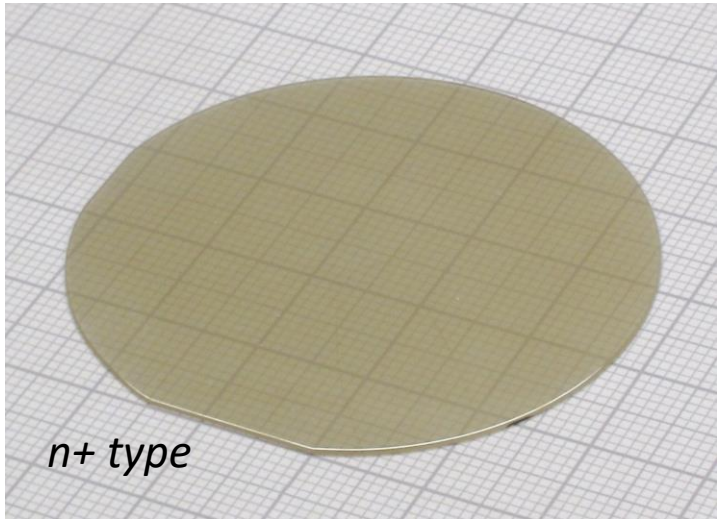
Front side			Epi-ready polished (RMS < 0,5 nm)
Back side			Ground

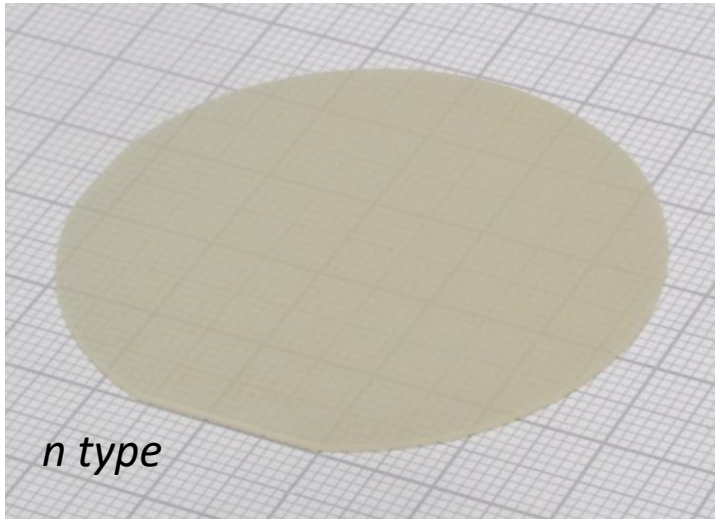
Steps of polishing:

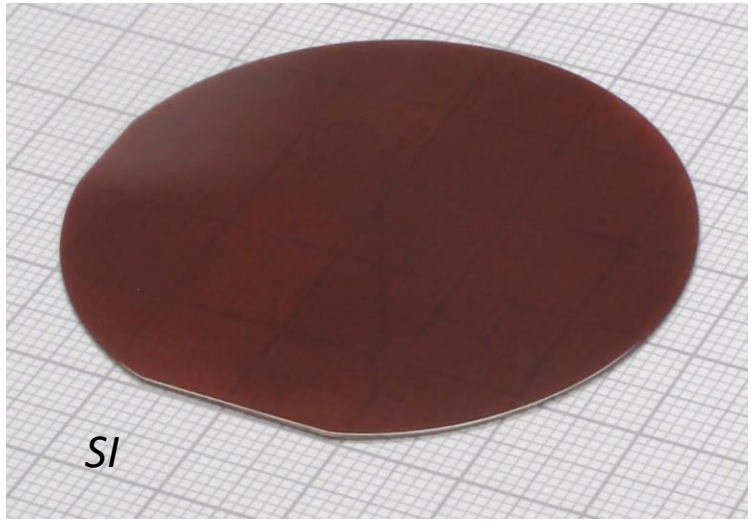
1. Grinding
2. Lapping
3. Polishing
4. Chemo-mechanical polishing



Am-GaN substrates – electrical properties

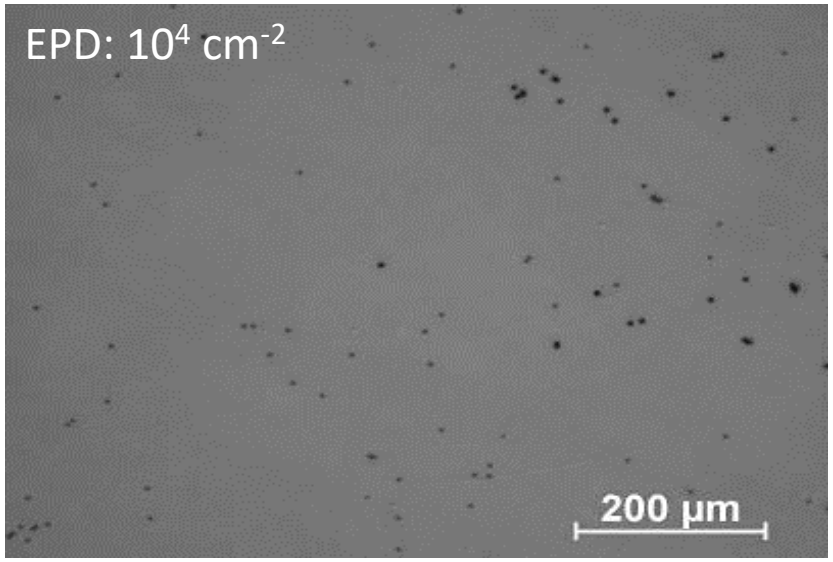




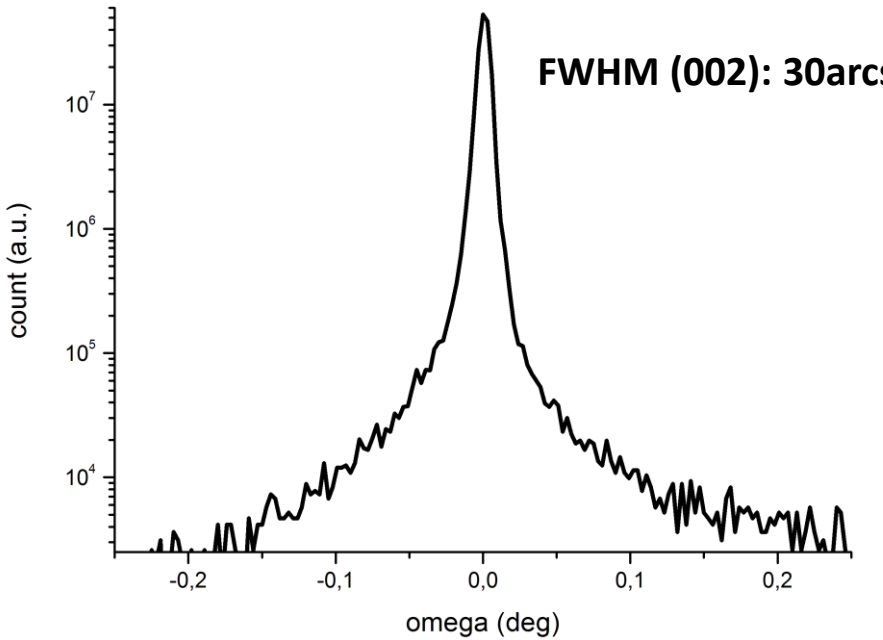


Material type	Conductivity type	Carrier concentration [cm^{-3}]	Carrier mobility [cm^2/Vs]	Resistivity [Ωcm]	Available size [inch]
High carrier concentration	n+ type	~10^{19}	~150	10^{-3}	1-2
Low carrier concentration	n type	~10^{18}	~250	10^{-2}	1-2
High resistivity (Mn-doped)	semi-insulating (SI)	-	-	≥10^{8}	1-1.5

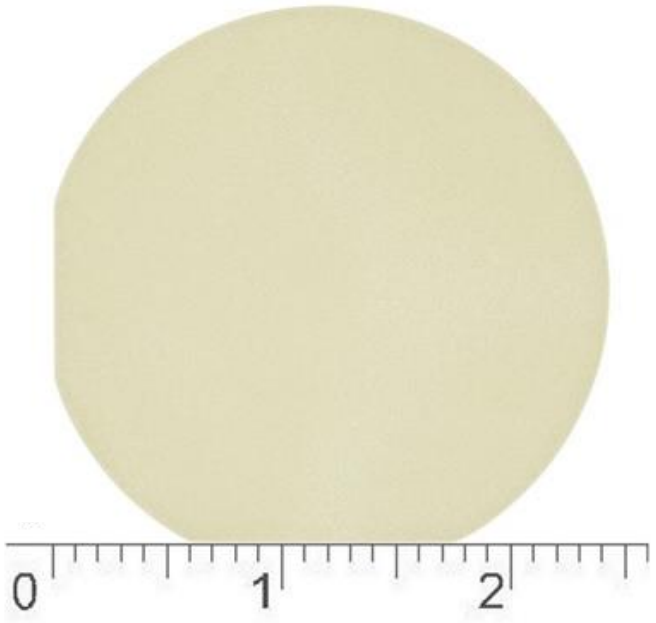
Am-GaN substrates – structural properties



Molten KOH+NaOH, 450°C



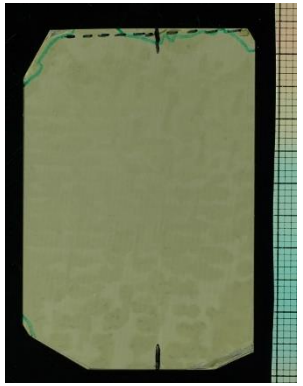
beam size: 1 mm x 10 mm



GaN substrate

Recent progress in ammonothermal method

seed

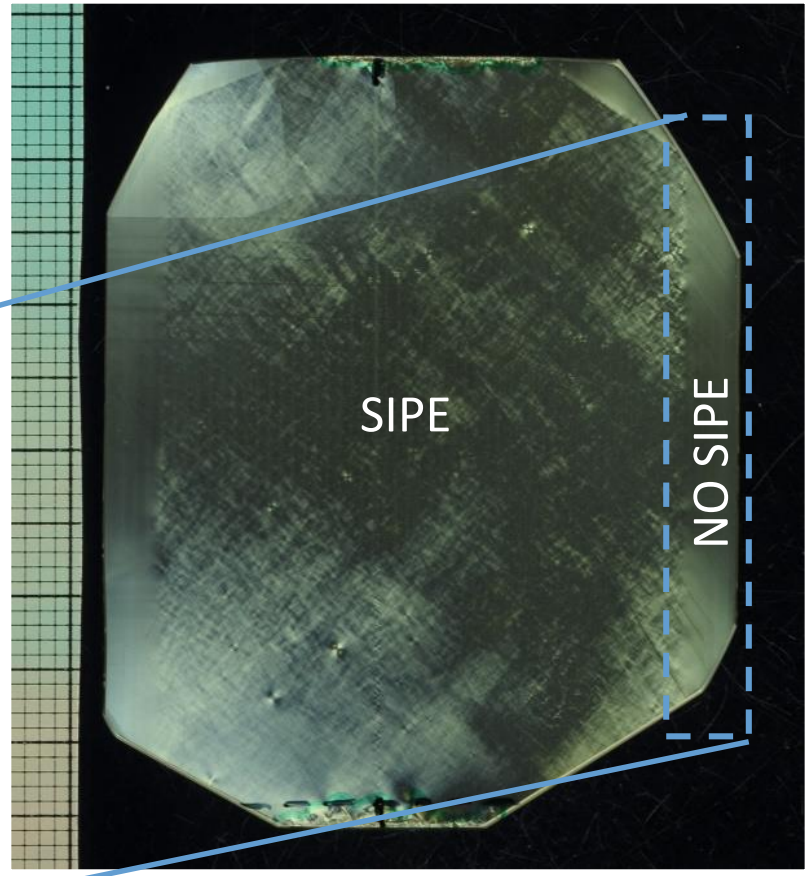


[10-10]

[11-20]

Crystals between crossed polarizers

1st growth run



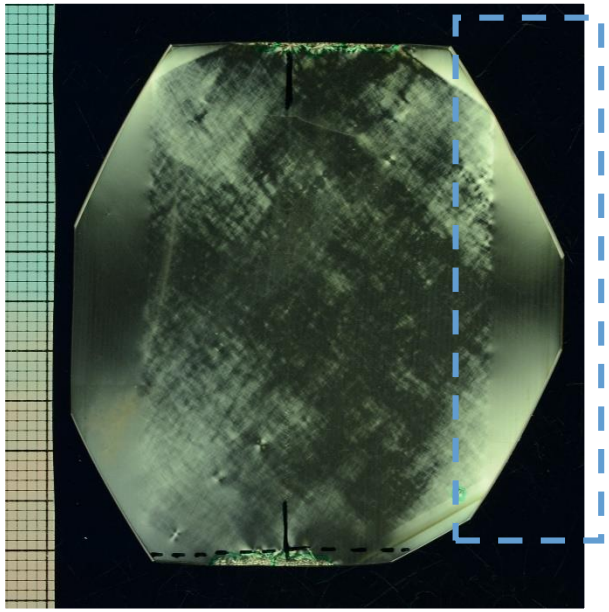
[000-1]

1st gr Am-GaN

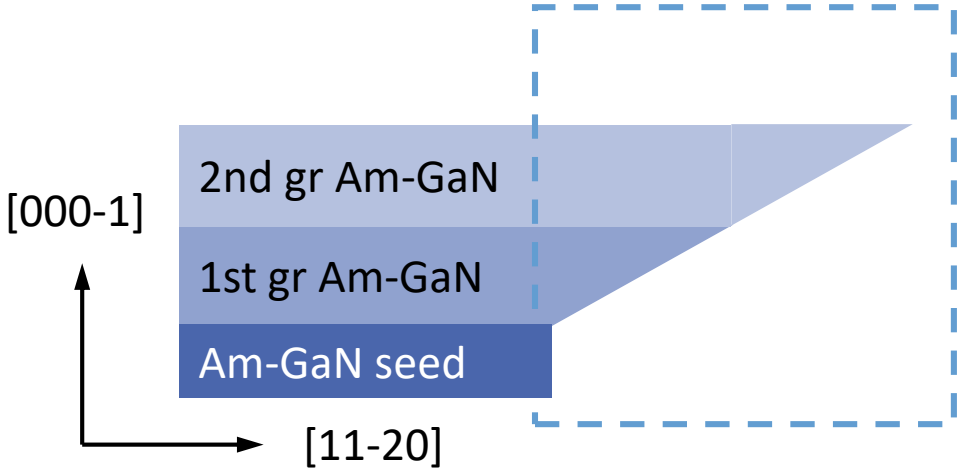
Am-GaN seed

[11-20]

Stress Induced Polarization Effect



2nd growth run

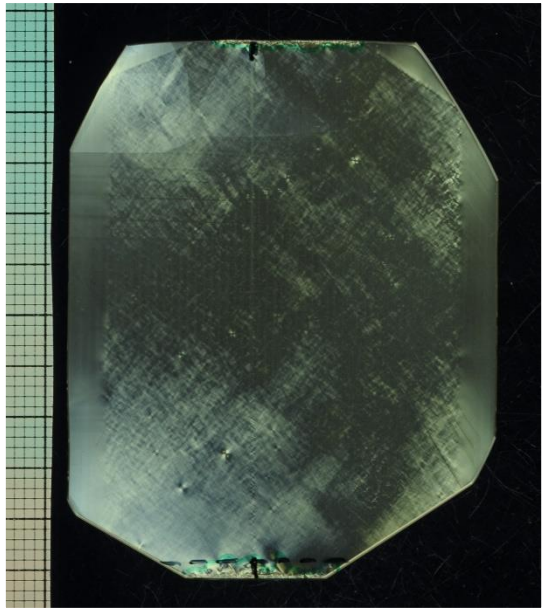


[10-10]

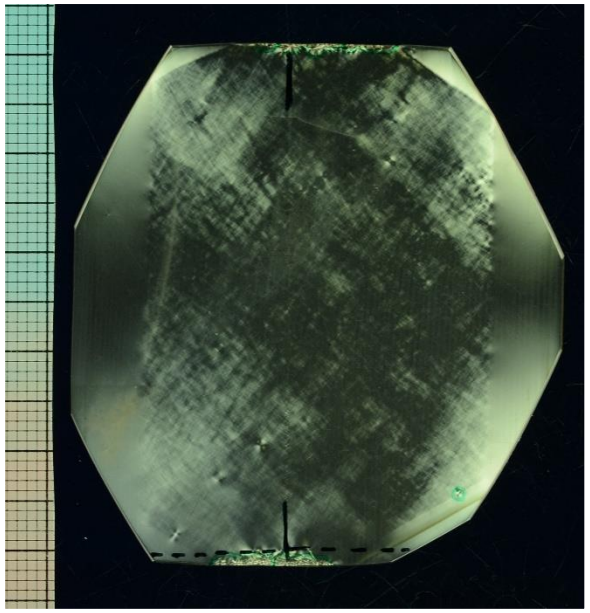
Crystals between crossed polarizers

[11-20]

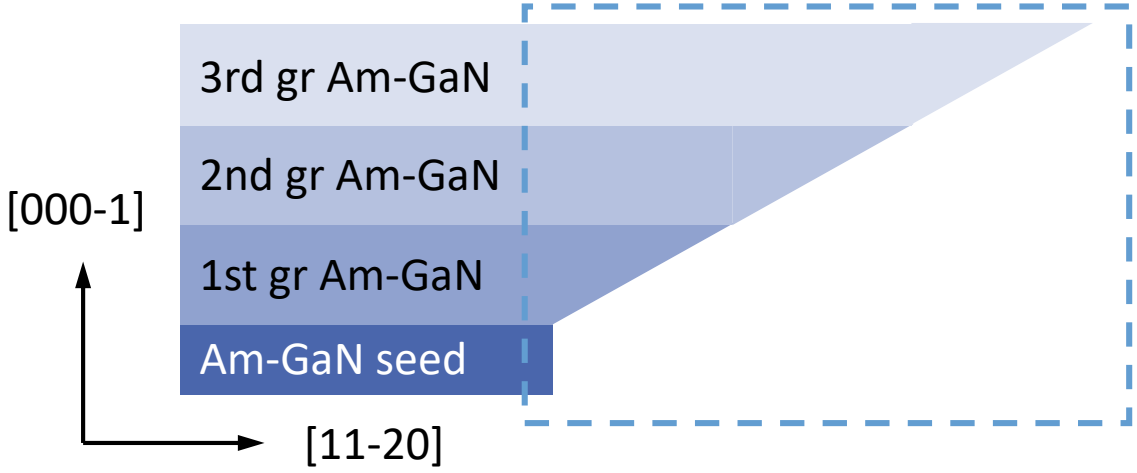
1st growth run



Stress Induced Polarization Effect



2nd growth run

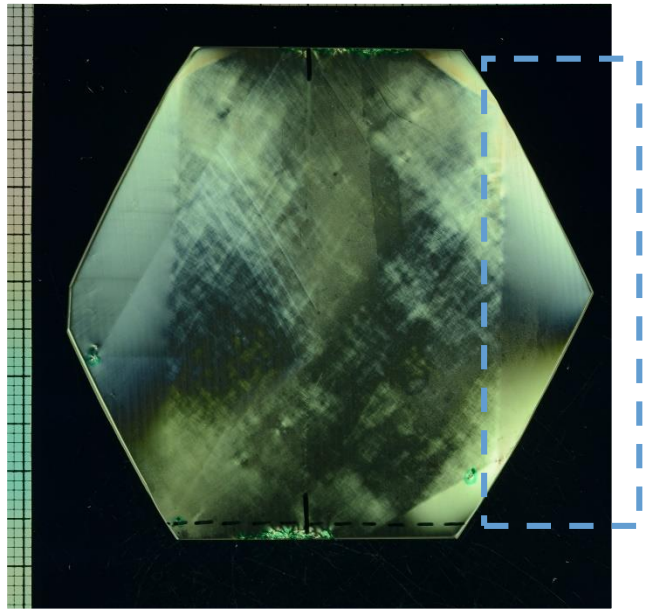


[10-10]

Crystals between crossed polarizers

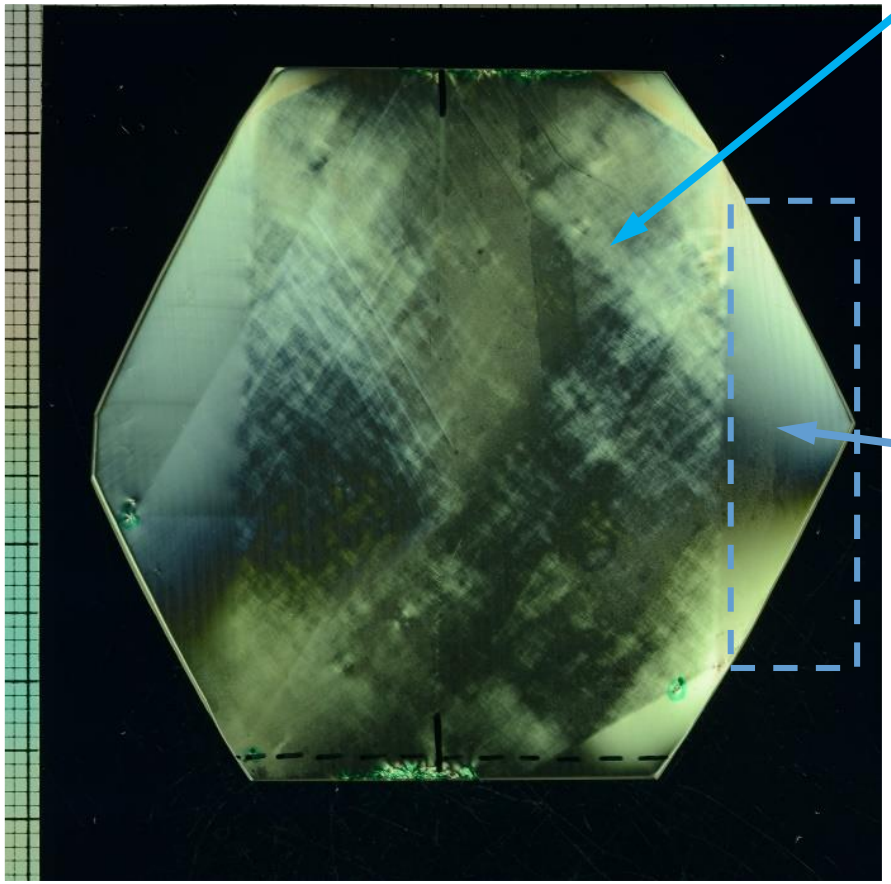
[11-20]

3rd growth run

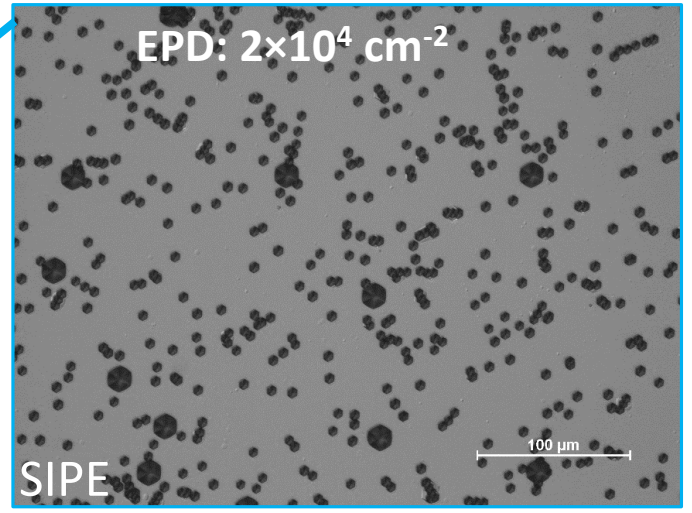


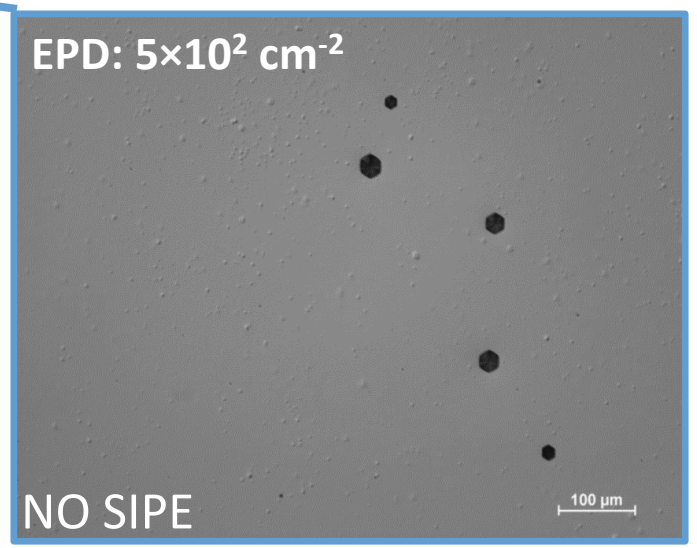
Stress Induced Polarization Effect

EPD after growth run of GaN



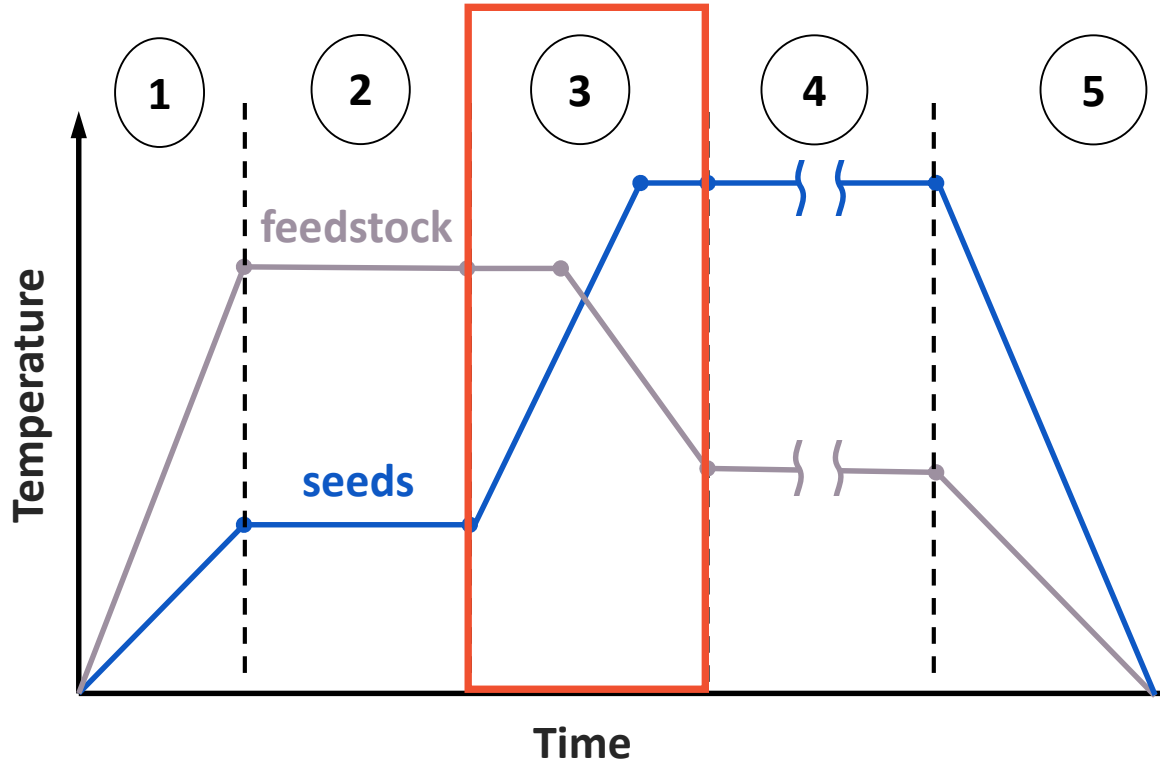
Molten KOH+NaOH
450°C

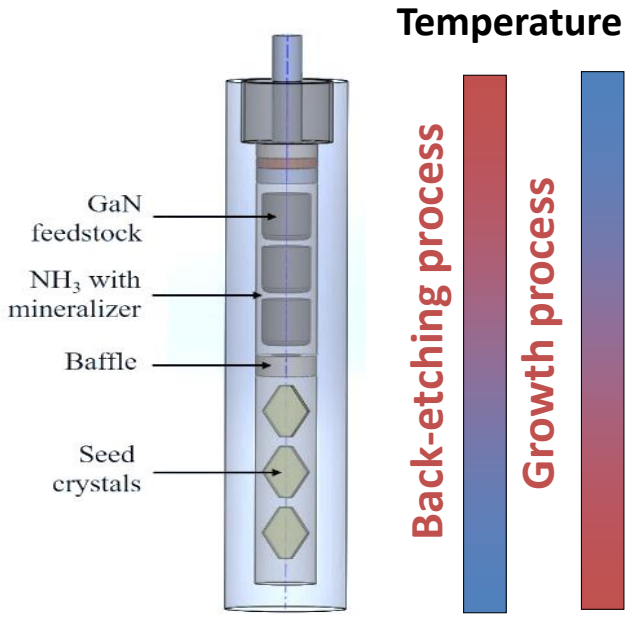




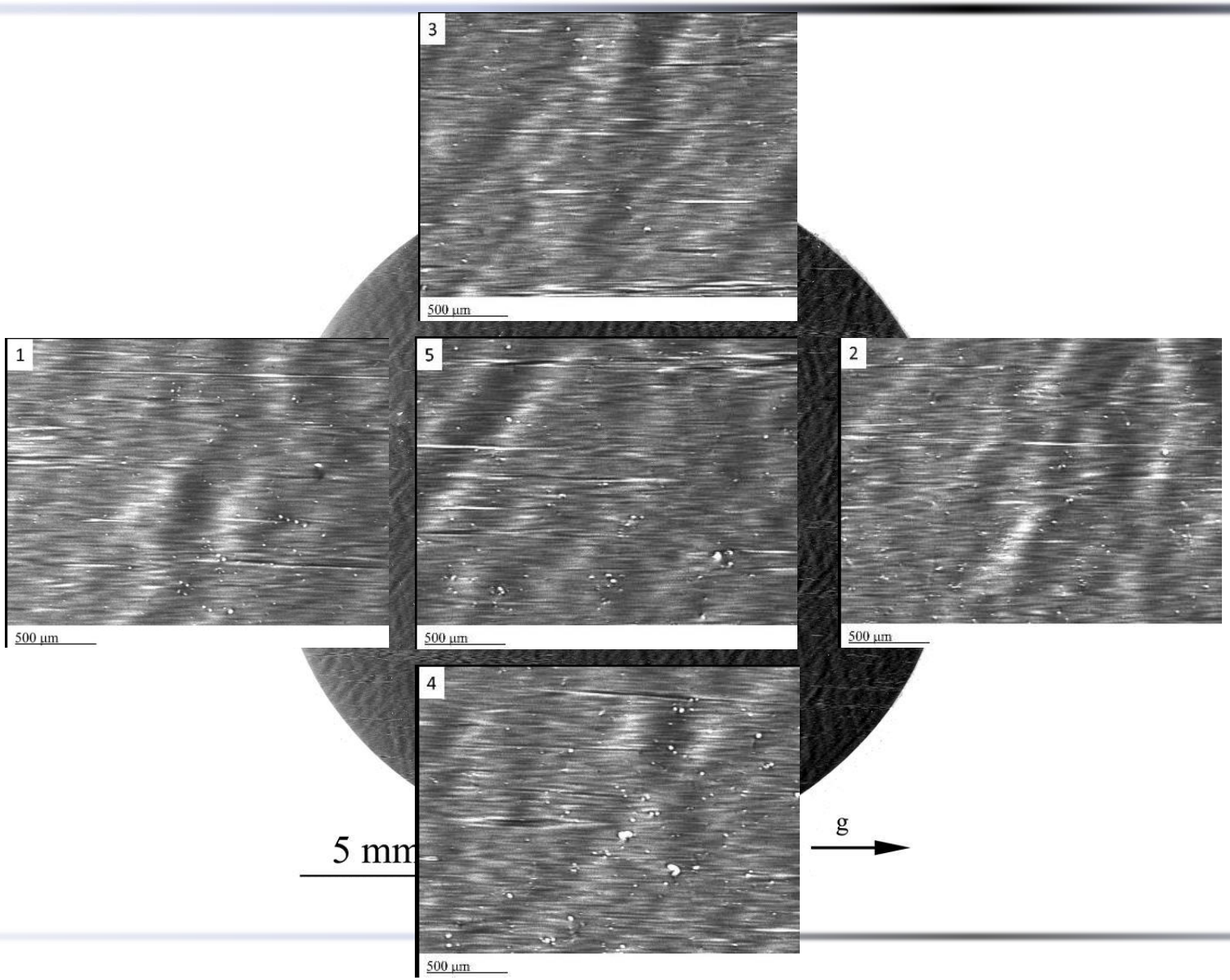
Basic ammonothermal method – process stages

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





Am-GaN - topography characterization



Synchrotron X-ray topography

(11-24) reflection

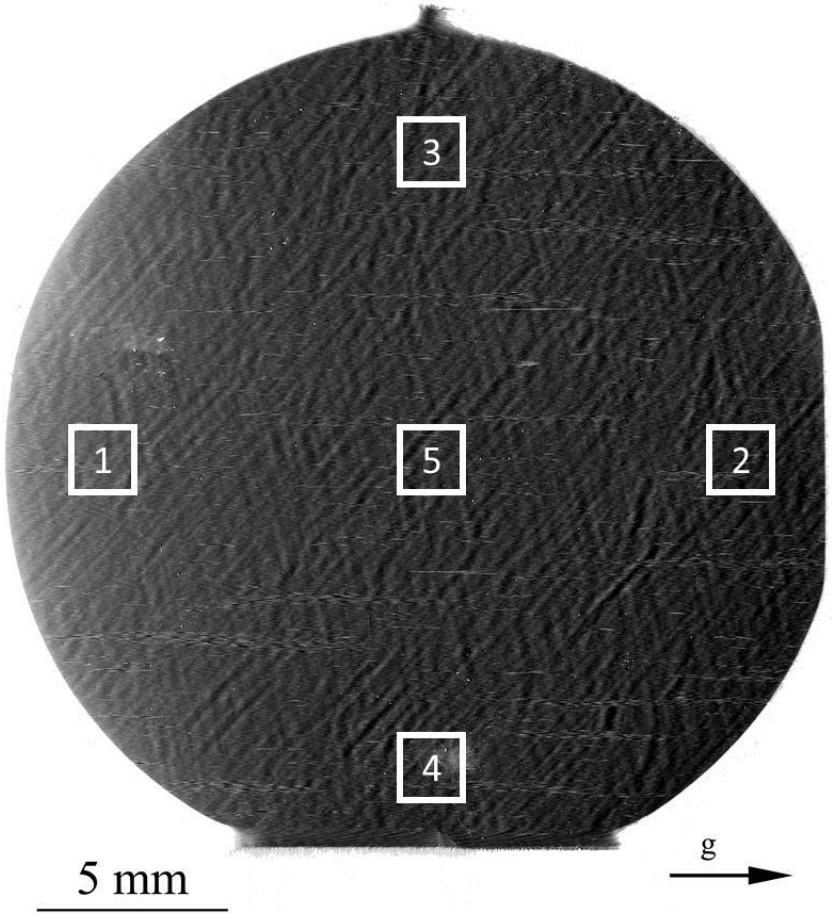
Region	Threading dislocation density [cm^{-2}]
1	5.9×10^3
2	6.5×10^3
3	3.6×10^3
4	5.2×10^3
5	4.6×10^3
Average	**5.2×10^3**

Liu, Y. et al., Journal of Crystal Growth , 125903.

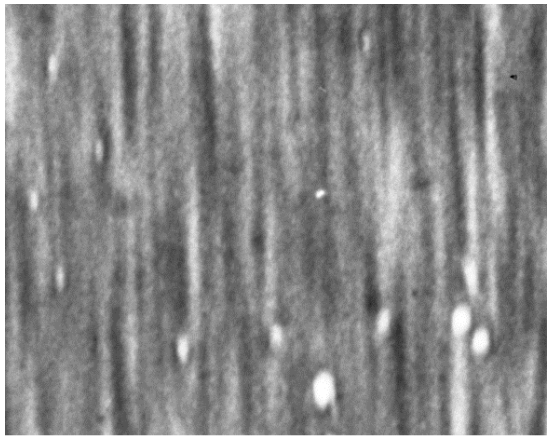
Am-GaN - topography characterization

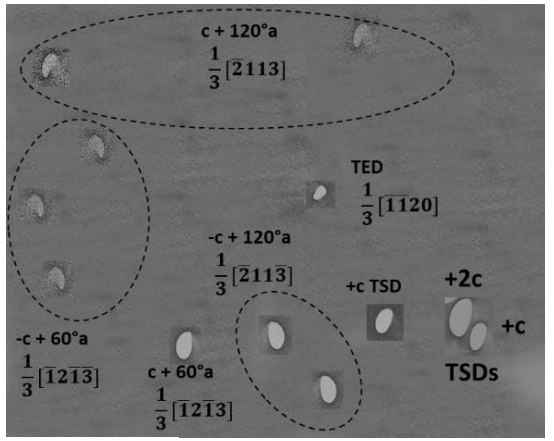
Synchrotron X-ray topography

(11-24) reflection



Region	TSD	TMD	TED
1	0.9%	95.2%	3.9%
2	0	97.3%	2.7%
3	0	98.6%	1.4%
4	1.5%	97%	1.5%
5	1.7%	93.9%	4.3%
Average	**0.8%**	**96.3%**	**2.9%**

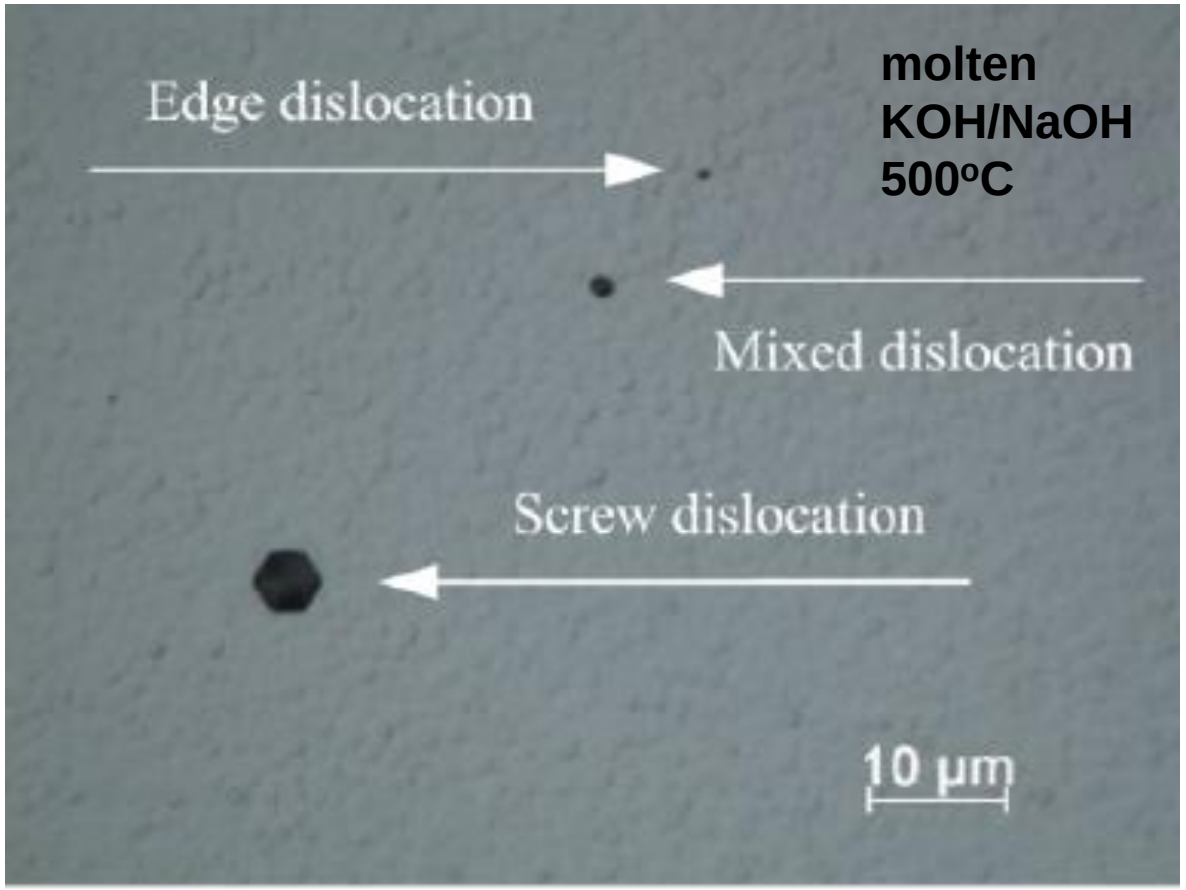


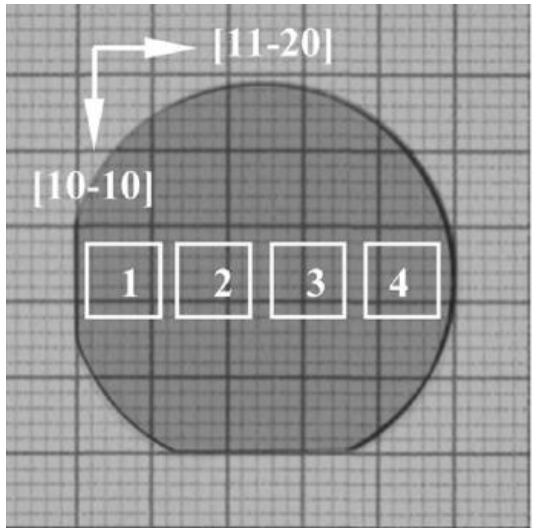


TSD – Threading Screw Dislocation
TMD – Threading Mixed Dislocation
TED – Threading Edge Dislocation

Liu, Y. et al., Journal of Crystal Growth , 125903.

Structural uniformity - etch pit distribution





Material	Am-GaN	Am-GaN	Am-GaN
Size of pits	small	medium	large
Area 1	1.7×10^4	2.9×10^4	1.0×10^0
Area 2	7.3×10^4	7.3×10^2	1.0×10^0
Area 3	2.5×10^4	4.4×10^3	1.0×10^0
Area 4	4.0×10^4	1.5×10^3	1.0×10^0
Average EPD	3.9×10^4	8.9×10^3	1.0×10^0

Largest pits are formed on screw dislocations, intermediate pits on mixed dislocations, and smallest on edge dislocations.

T. Sochacki et al., Japanese Journal of Applied Physics 58, SCCB19 (2019).


Crystals after growth process

Summary

- The main advantage of the ammonothermal technique is the possibility to grow high-diameter crystals with excellent structural properties.
- Tiling technology is a new way to produce larger crystals.
- Growth of ammonothermal GaN crystals with EPD of the order of 10^2 cm^{-2} is possible.
- Proper growth conditions, in terms of temperature distribution and controlled transition between back-etching and growth stage, allow to maintain EPD at an extremely low level – possible way for creation of new generation of seeds.

Plans for the future

- Increasing the size of seeds with and without tiling technology.
- SIPE analysis and improvement of the quality of seeds and substrates.
- Tests of new internal configurations: crucibles, baffle.
- Numerical modeling of convection inside the autoclave.

Acknowledgements

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