HVPE-GaN growth On the bumpy road to bulk GaN and high quality wafers

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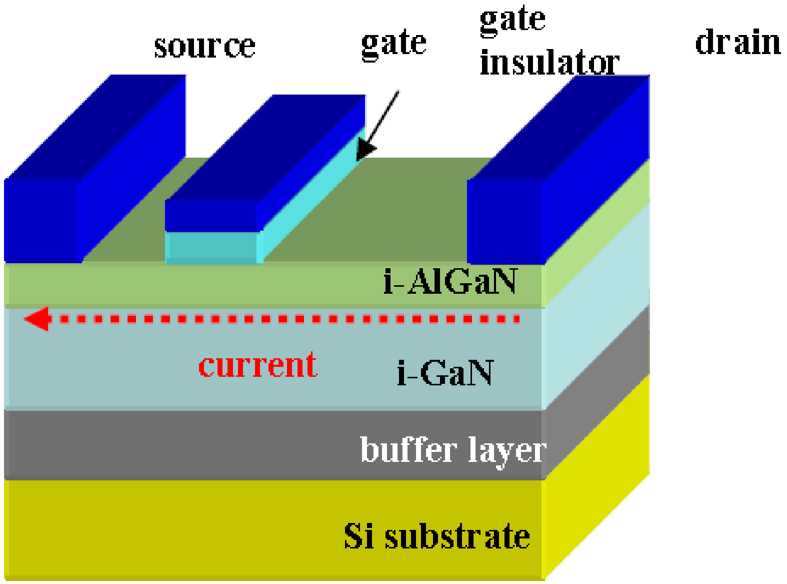
Do we need GaN substrates?

Decorative lighting

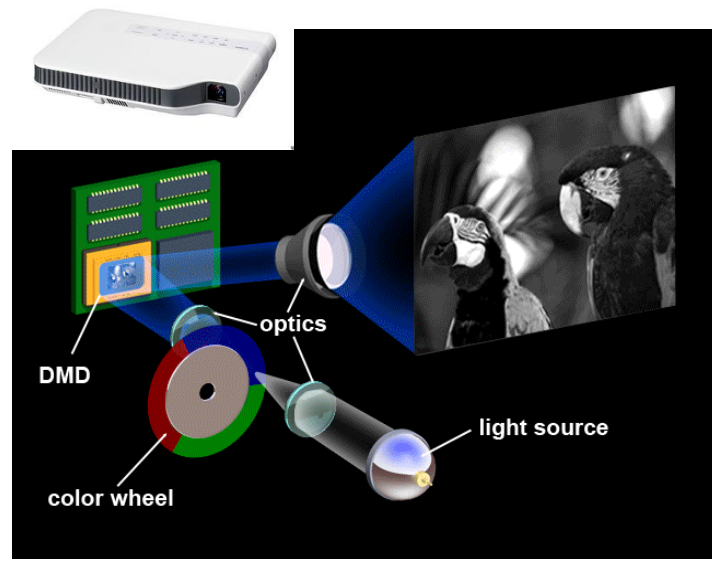
Indoor lighting



T. Uesugi, T. Kachi, CS MANTECH Conference, May 16th-19th, 2011, Palm Spring, CA, USA

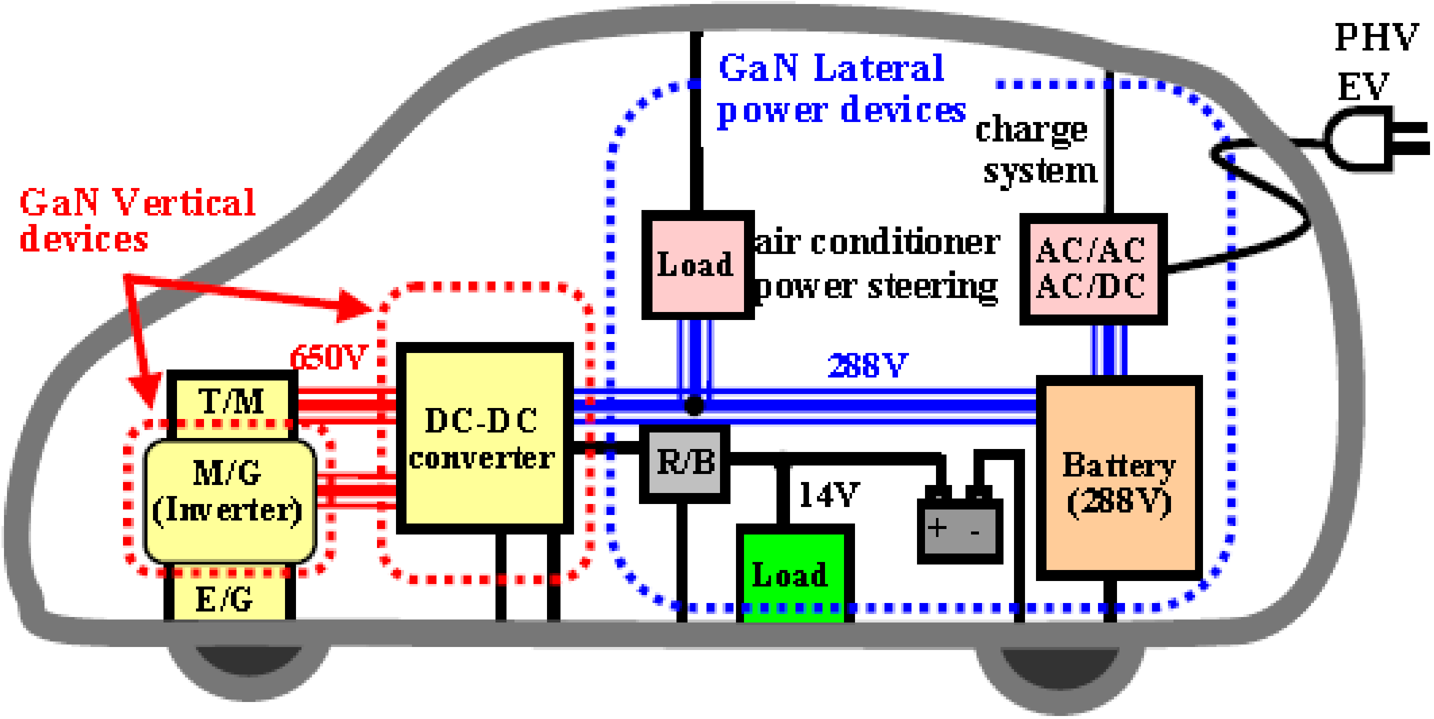
Do we need GaN substrates?

Blu-ray Disc™



http://jalopnik.com/how-bmws-new-laser-headlights-will-work-and-not-kill-y-1521586271

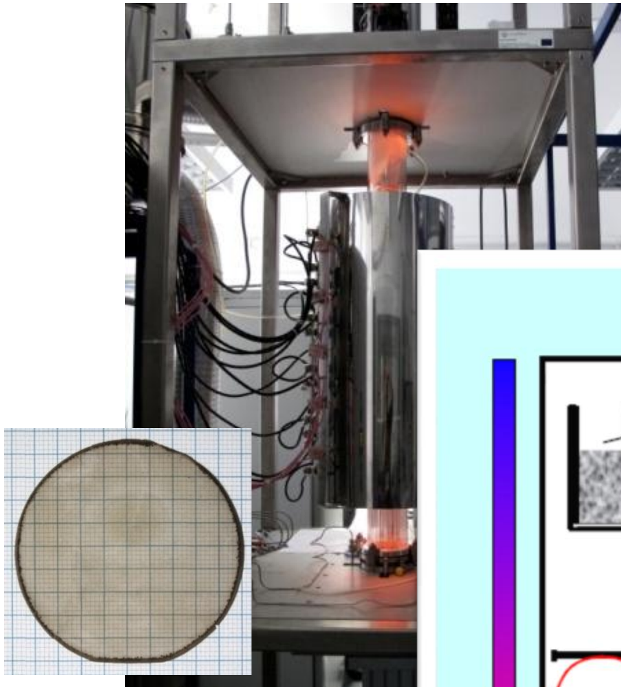
Do we need GaN substrates?

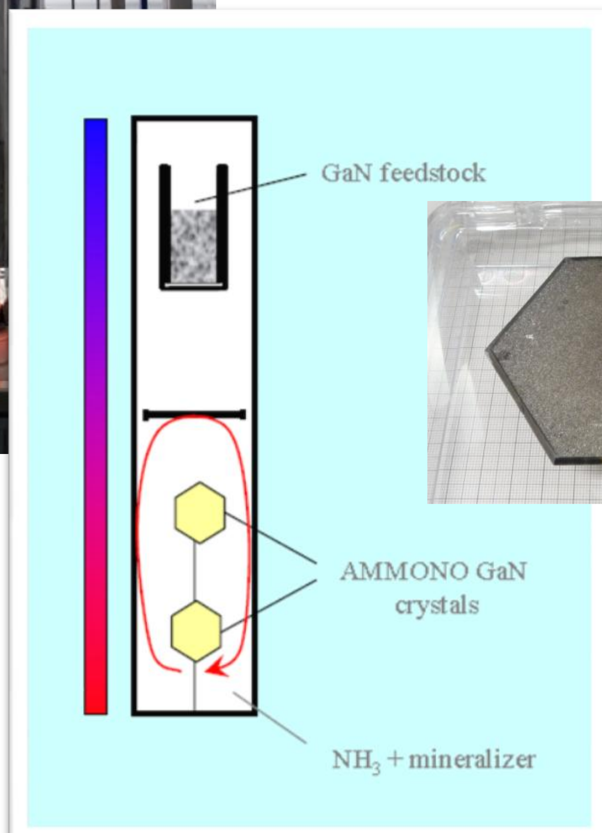


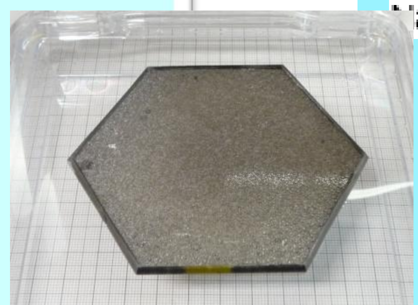
T. Kachi, Japanese Journal of Applied Physics 53, 100210 (2014)

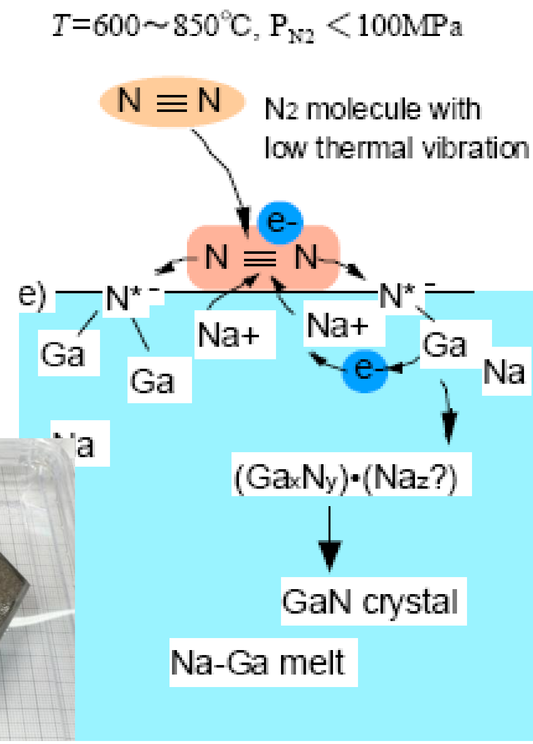
T. Uesugi, T. Kachi, CS MANTECH Conference, May 16th-19th, 2011, Palm Spring, CA, USA

GaN growth methods

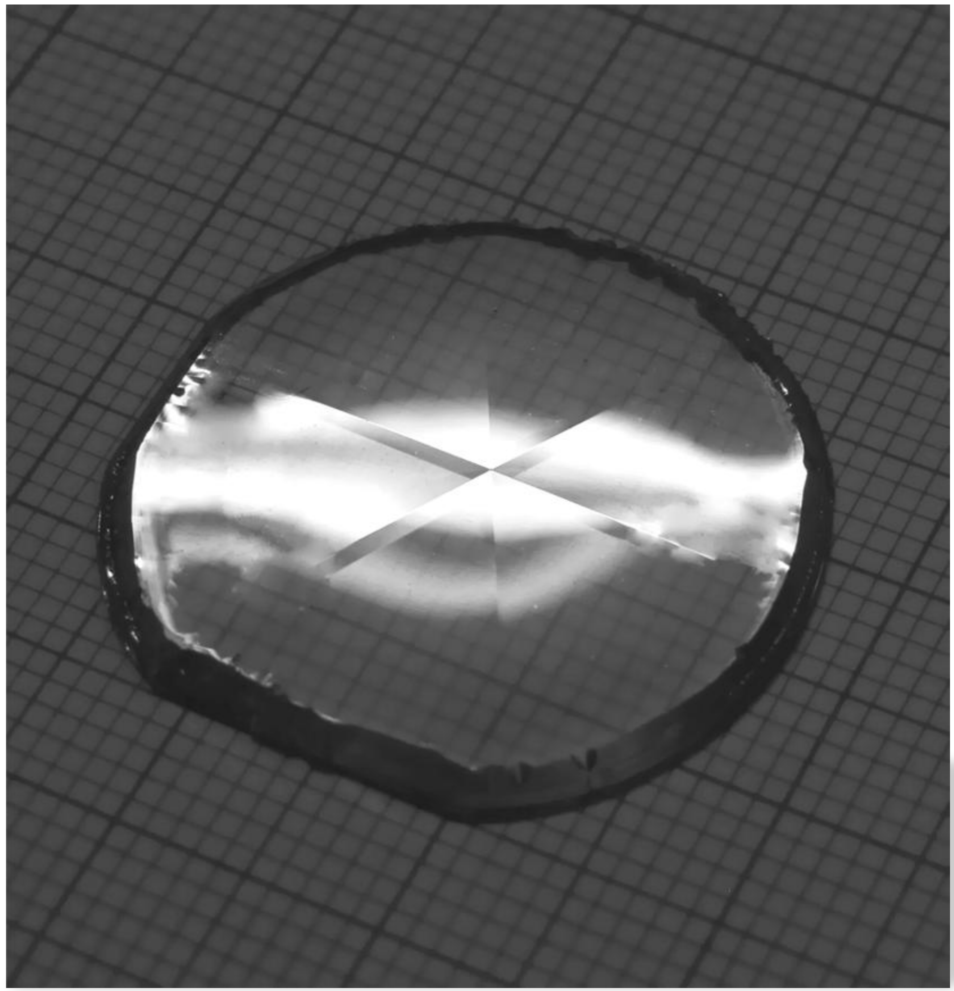








Hydride Vapor Phase Epitaxy (HVPE growth method)



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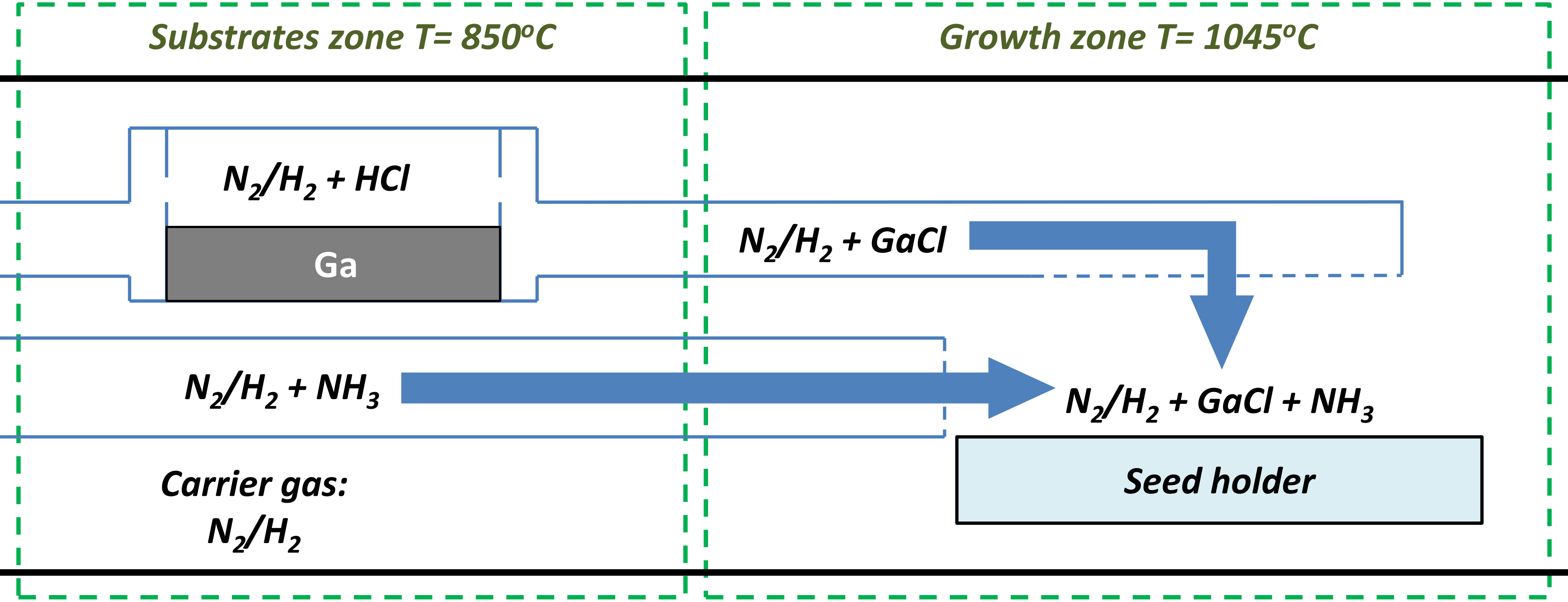
HVPE method

$$2HCl_{(g)} + 2Ga_{(l)} = 2GaCl_{(g)} + H_{2(g)}$$

$$GaCl_{(g)} + 2HCl_{(g)} = GaCl_{3(g)} + H_{2(g)}$$

$$GaCl_{(g)} + NH_{3(g)} = GaN_{(s)} + HCl_{(g)} + H_{2(g)}$$



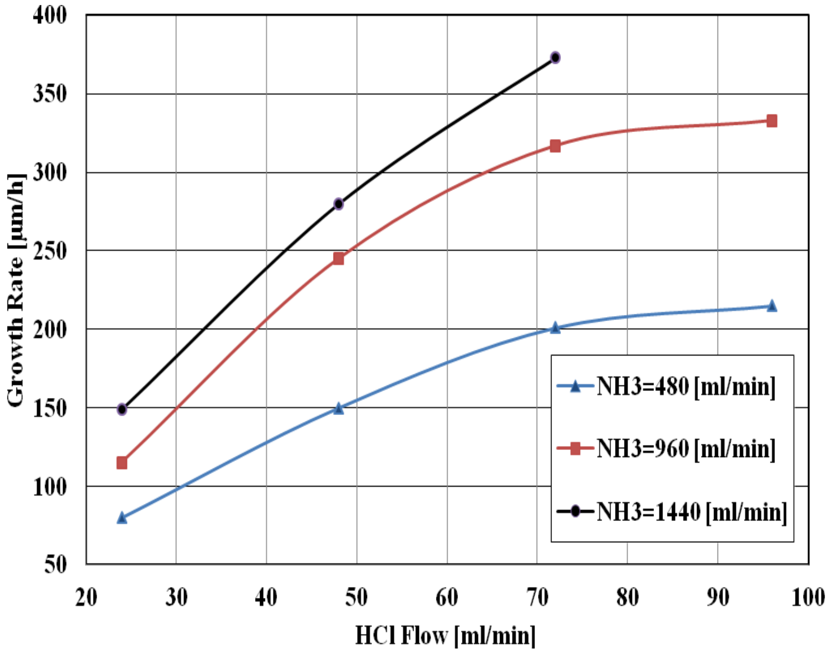
$$\Delta P_{Ga} = [P^{\circ}_{GaCl} - (P_{GaCl_3} + P_{GaCl})]$$ ***at ammonia rich conditions***

A. Koukitu, Y. Kumagai in Technology of Gallium Nitride Crystal Growth, Springer-Verlag, 2010, p. 31.

Advantages of HVPE method

High growth rate (>100 µm/h)

c-plane



High purity
(impurities concentration < 10^{16} cm^{-3})
c-plane

Doping with Si or Ge

$n = 5 \times 10^{18}$ cm^{-3}

$\mu = 170$ [cm^2/Vs]

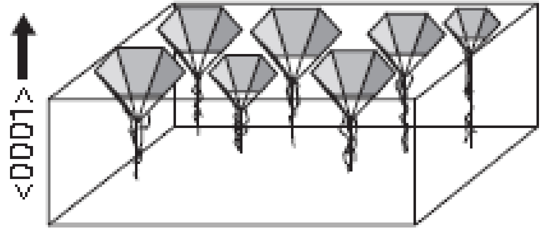
Doping with C or Fe

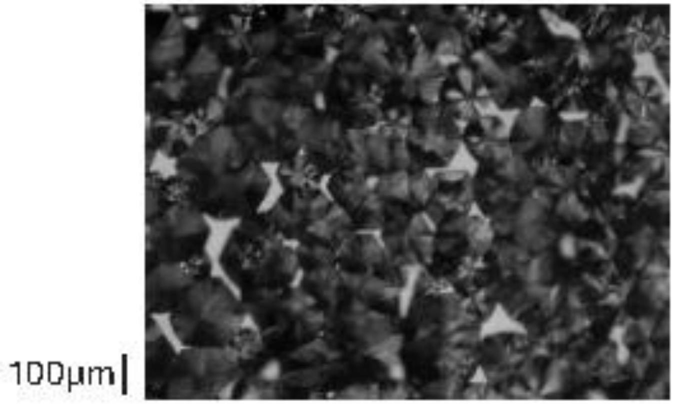
semi-insulating

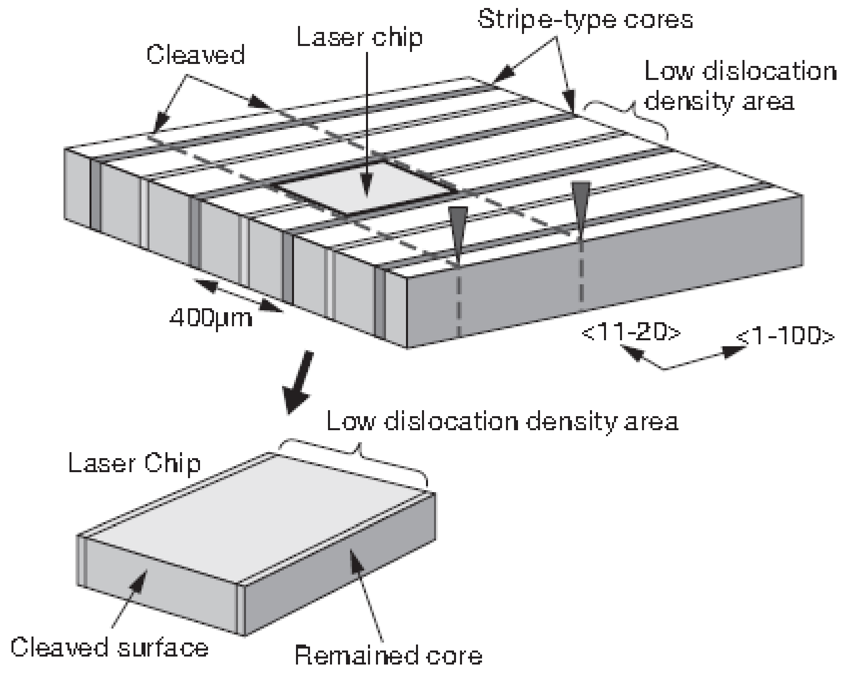
T. Sochacki et al. Journal of Crystal Growth 407 (2014) 52–57

Commercially available HVPE-GaN

Growth on GaAs (111)A/LT GaN by Dislocation Elimination by the Epitaxial growth with inverse pyramidal Pits (DEEP) and Advanced-DEEP (A-DEEP)







K. Motoki, et.al, J. Cryst Growth 237 (2002) 912; J. Cryst Growth 305 (2007) 377

K. Motoki, SEI Technical Review, Number 70, April 2010; 28

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HVPE-GaN substrates suppliers

SUMITOMO CHEMICAL

http://www.hitachi-metals.co.jp

MOCVD-GaN/sapphire

MITSUBISHI CHEMICAL

http://www.m-kagaku.co.jp

FURUKAWA

http://www.furukawakk.co.jp

AETech

http://www.aetech.jp/

SAINT-GOBAIN

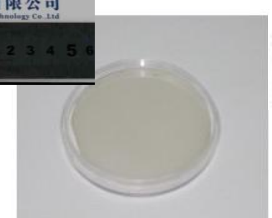
http://www.lumilog.com

Nanowin

http://www.nanowin.com.cn

kyma technologies

http://www.kymatech.com

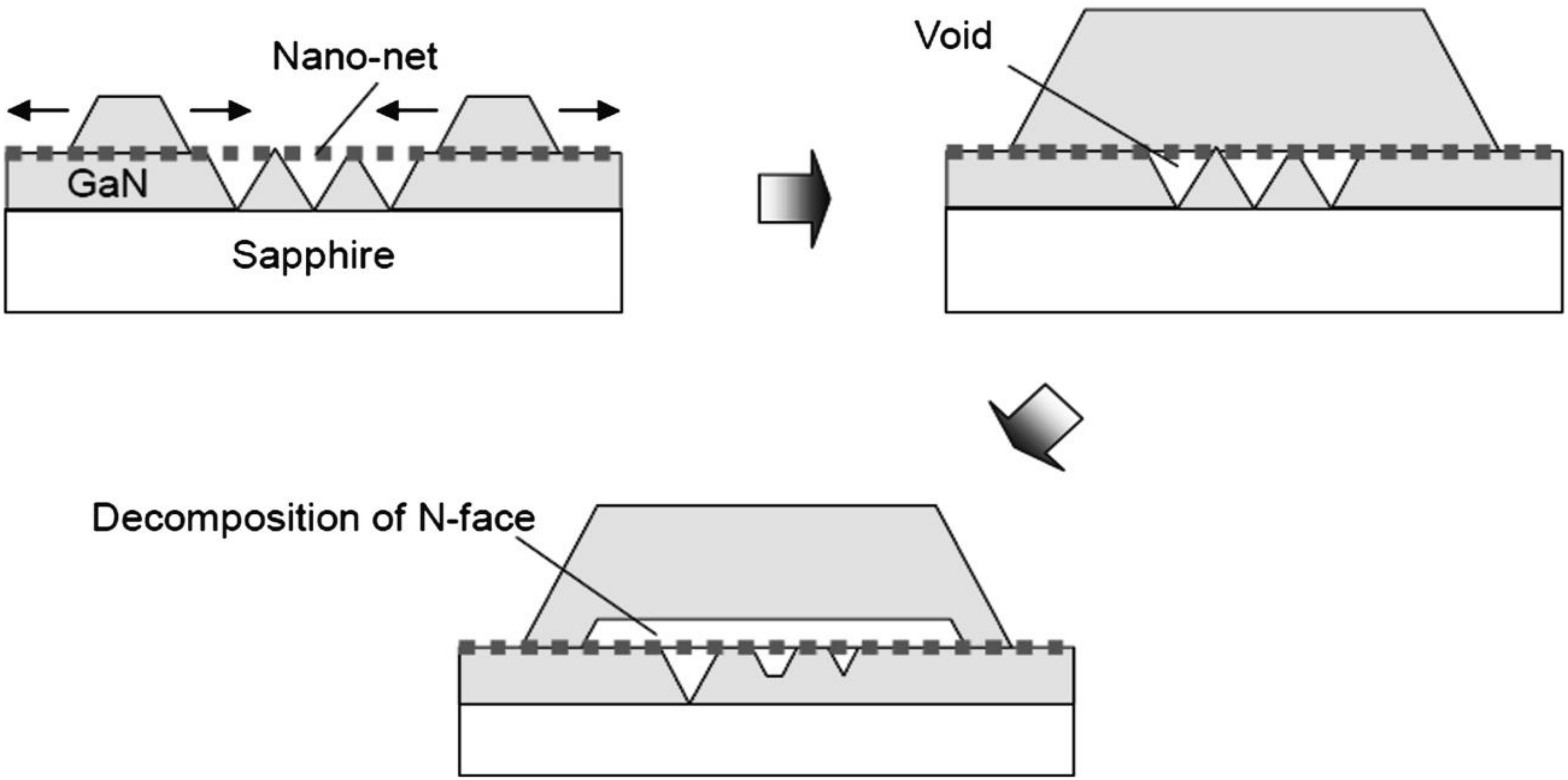


sinonitride.com

http://www.sinonitride.com

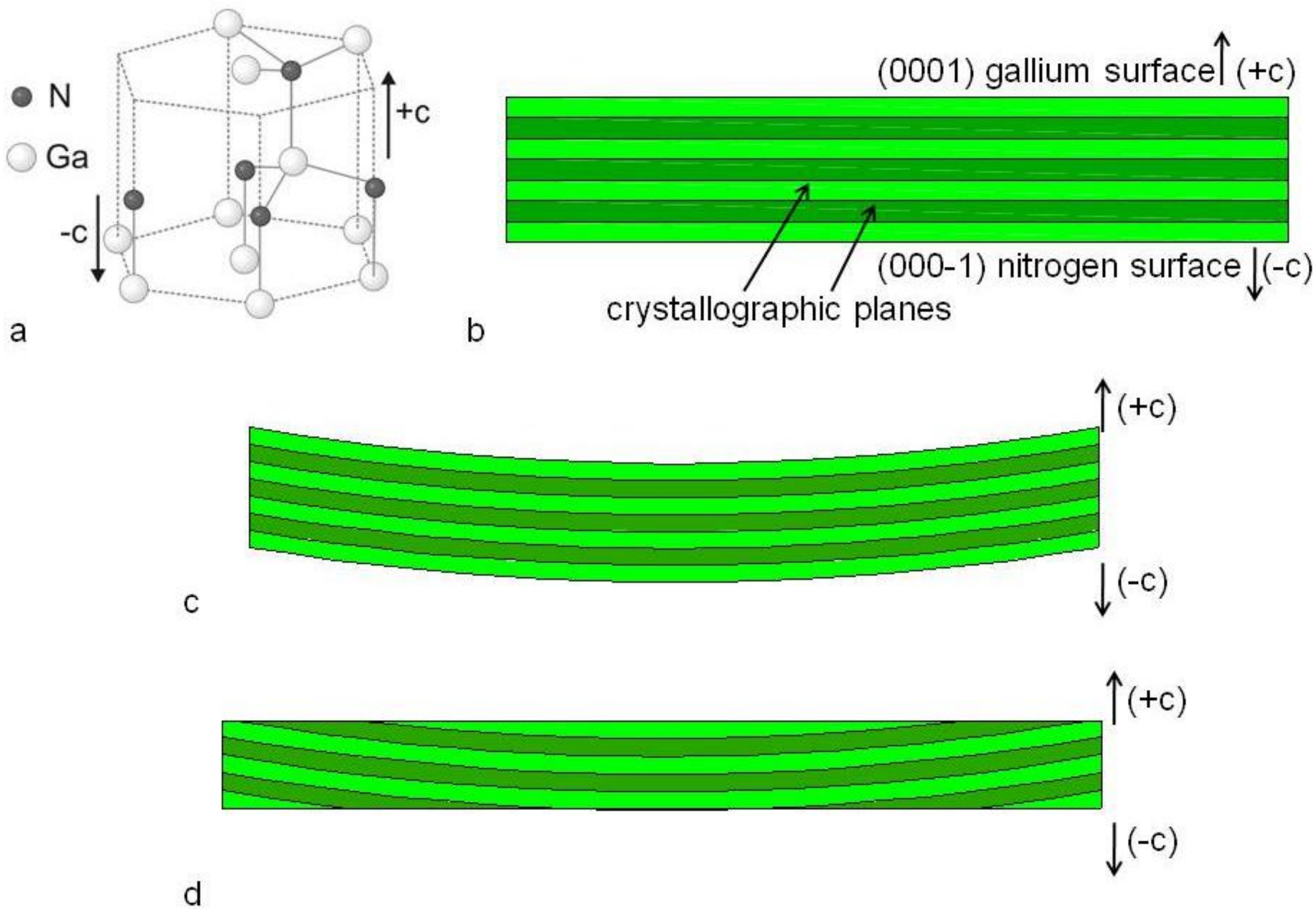
HVPE-GaN substrates suppliers

Growth on sapphire/MOVPE-GaN/Ti by Void-Assisted Separation



Y. Oshima et al. Jpn. J. Appl. Phys. V. 42 (2003)

Bending of crystallographic planes



Bending of crystallographic planes

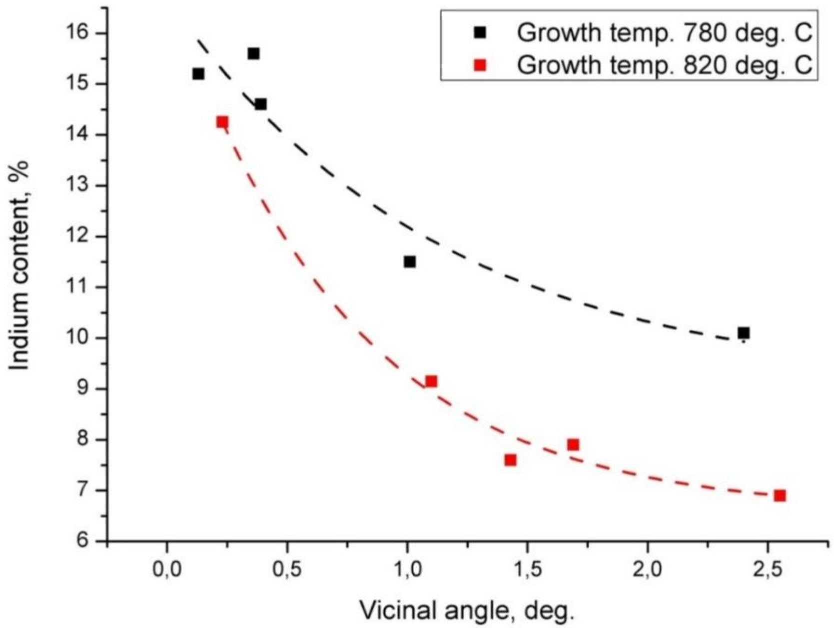
The wafer's surface needs to be offcut uniformly for 0.1 degree in a specific direction:

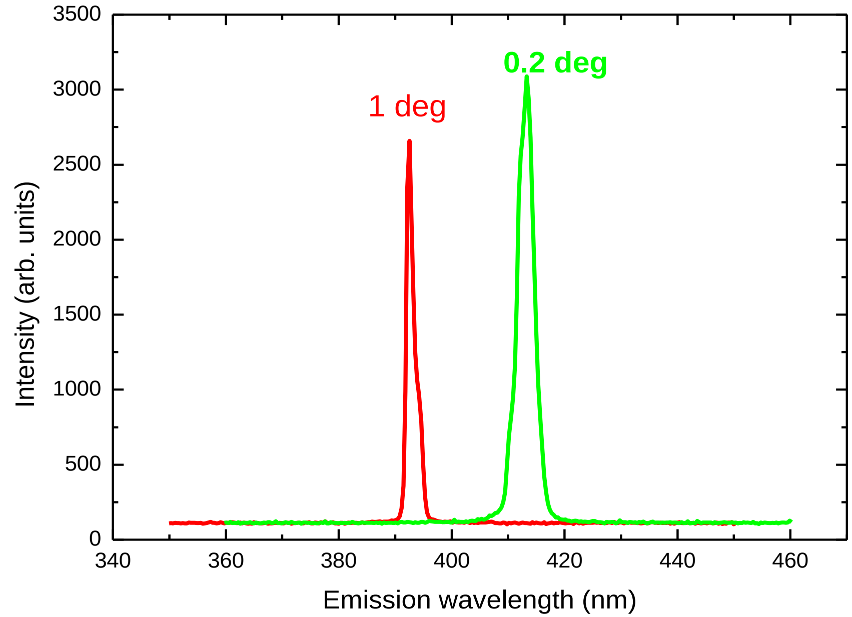
-to promote bilayer step flow,
-to control the composition of ternary alloys in device layers,
-to control the incorporation of dopants and unwanted impurities.

Calculated miscut deviation over the wafer for different bow radii				
Wafer Dia	*Lattice Bow Radius*			
	5 m	*10 m*	*20 m*	*30 m*
1”	*0.3°*	*0.15°*	*0.07°*	*0.05°*
2”	*0.6°*	*0.3°*	*0.15°*	*0.1°*
3”	*0.9°*	*0.5°*	*0.2°*	*0.15°*
4”	*1.6°*	*0.6°*	*0.3°*	*0.2°*

M. Boćkowski and Z. Sitar, CS Vol. 20 Issue 4 (2014) 48-51

Free-standing HVPE-GaN substrate
Uniform offcut required!

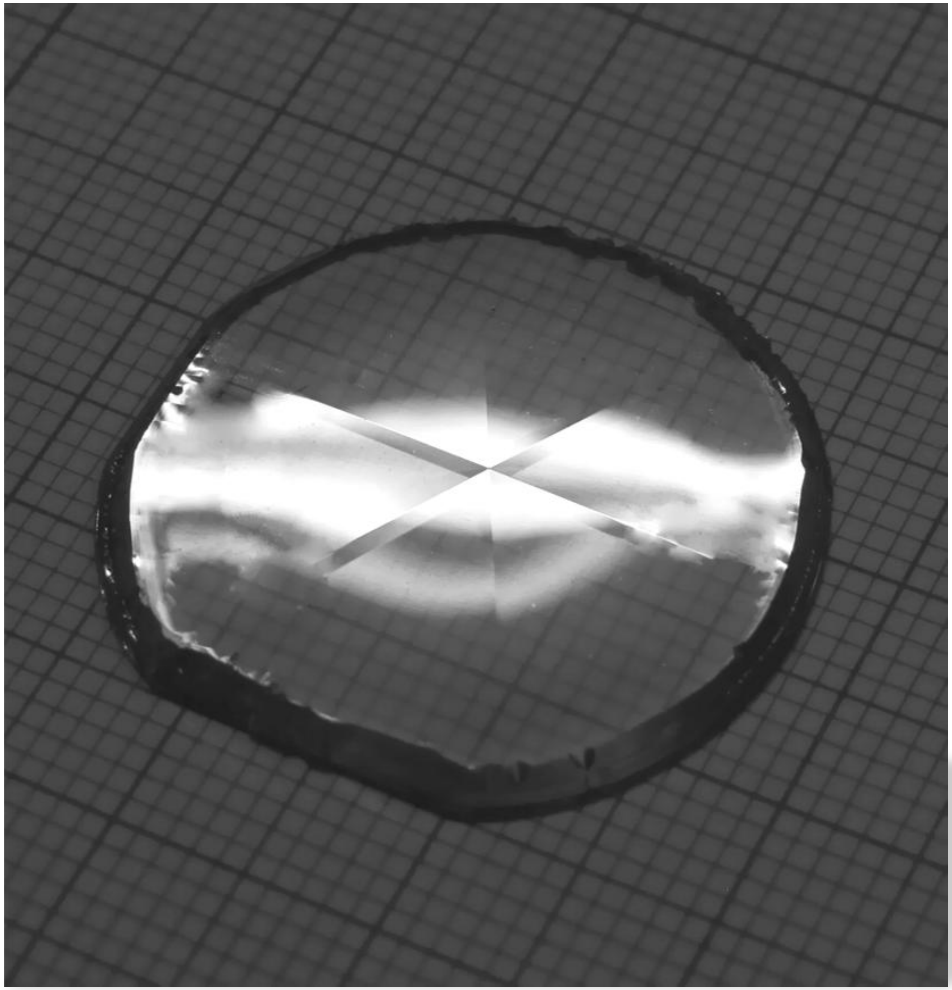




T. Suski et al., Applied Physics Letters Vol. 93 Issue: 17, 172117, 2008

unipress

Na-flux growth method



Na-flux growth method

Discovered by Prof. Yamane at Tohoku Univ. 1997

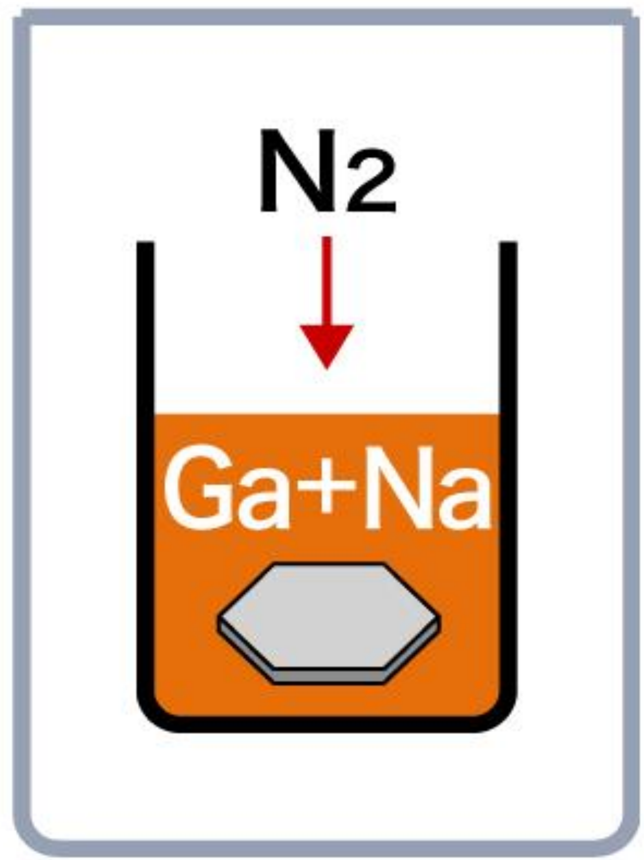
Developed by Prof. Mori at Osaka Univ.

N_2 pressure < 100 MPa and temperature < 900^{o}C

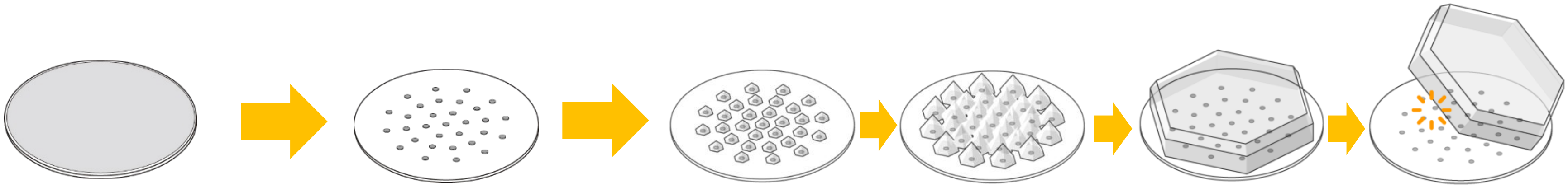
Growth rate - 50 µm/h

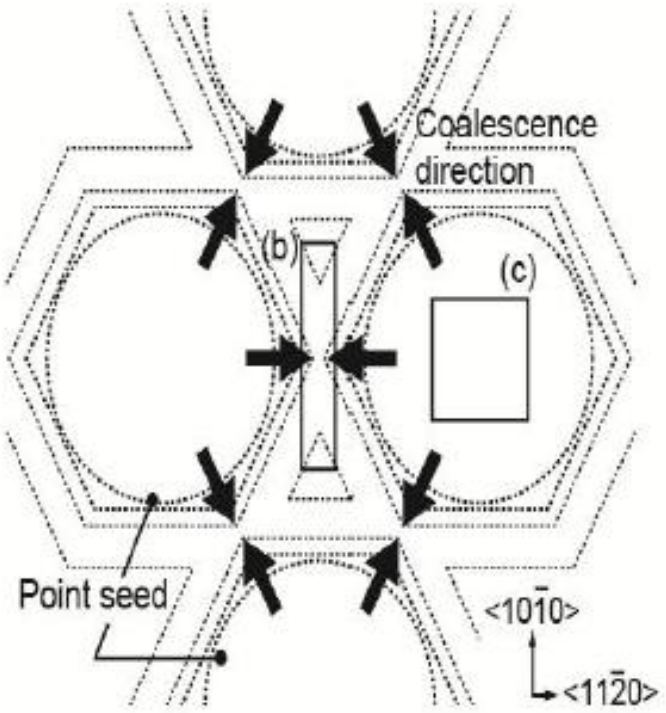
Growth run proceeds at constant temperature

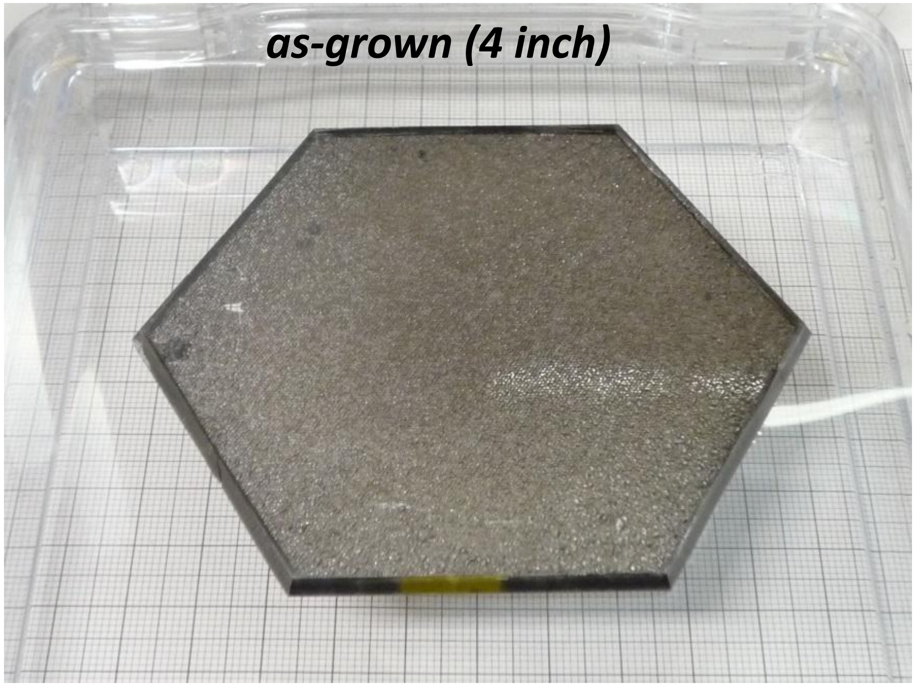
The mass transport is governed by convection caused by mechanical stirring of the flux



Growth by the Na-flux
Point Seed Technique (SPST)



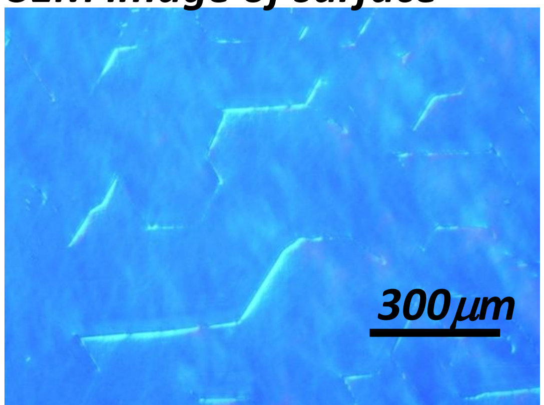


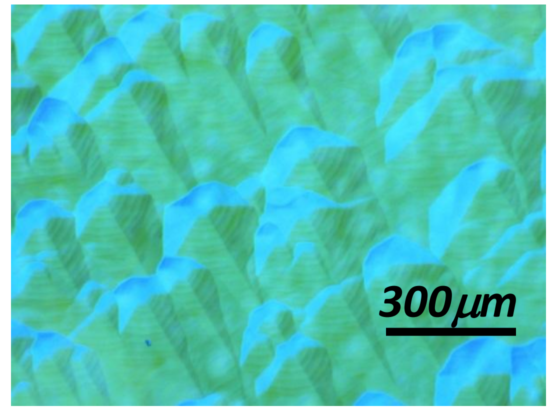


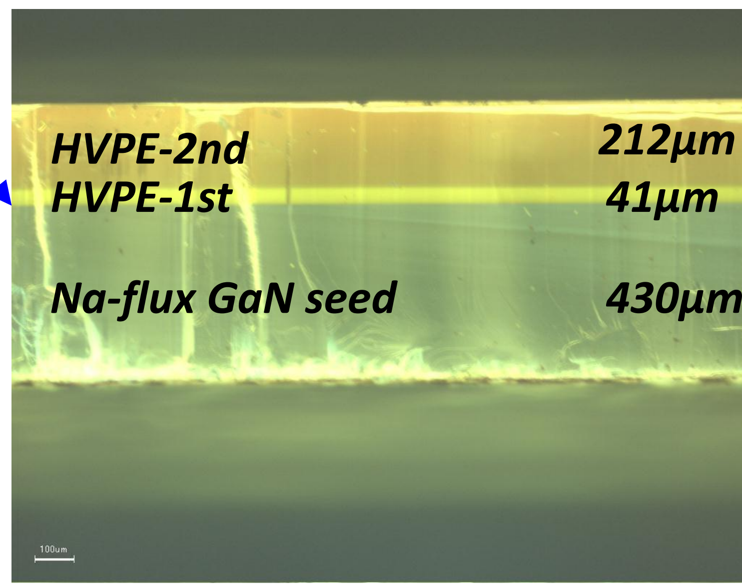
Y. Mori et al., CS MANTECH Conference, May 19th - 22nd, 2014, Denver, Colorado, USA

GaN crystal by HVPE on coalesced GaN seed

SEM image of surface







Growth rate: ~80µm

Y. Mori et al., IWN 2014 Conference, August 24th – 29th, 2014, Poland

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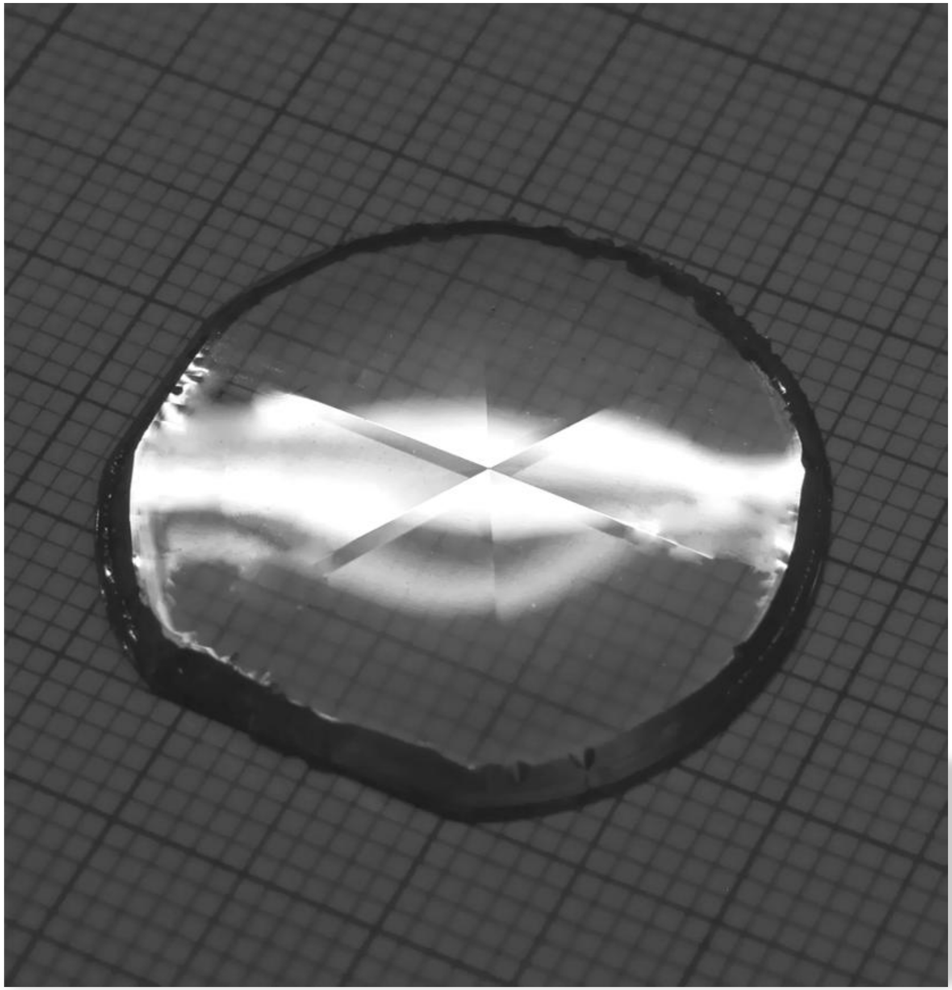
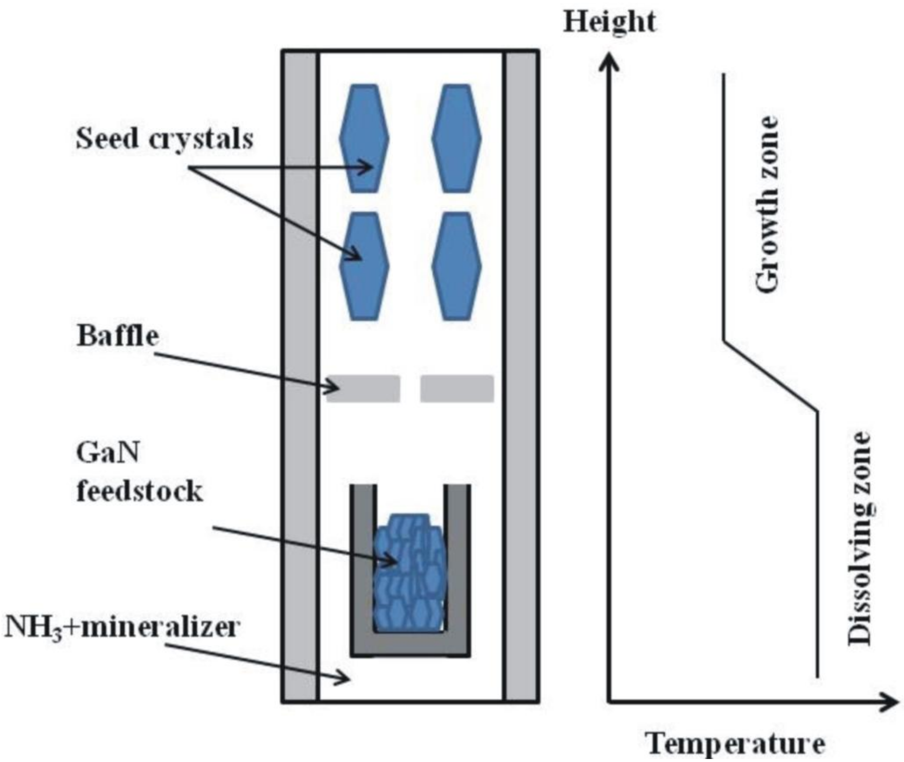
Ammonothermal growth method

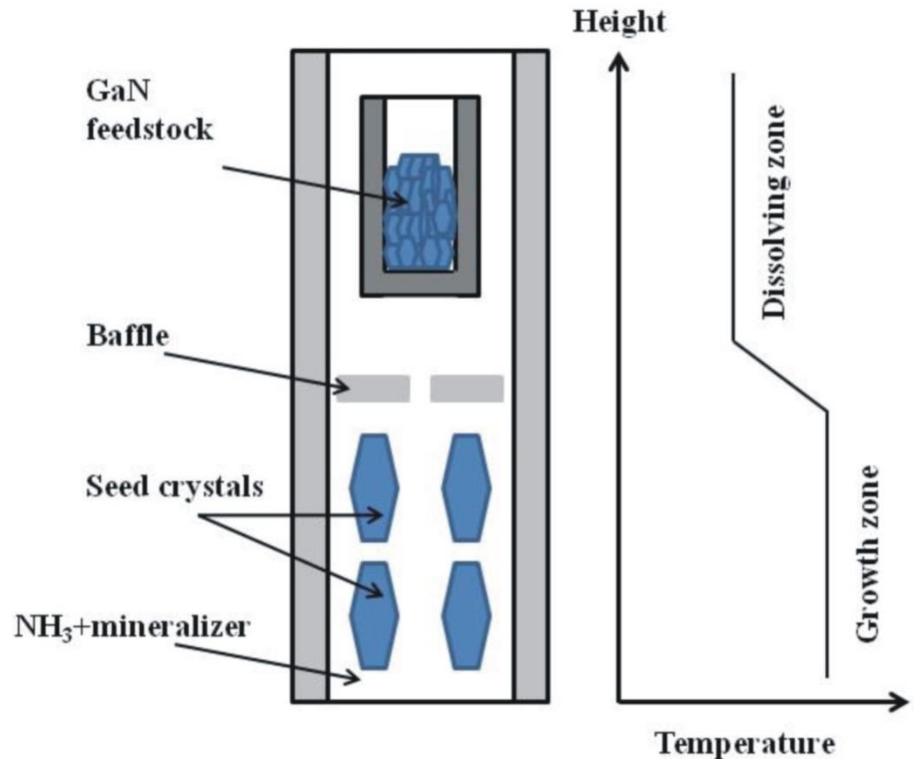


Ammonothermal method

- ***analogous to hydrothermal crystallization of quartz or oxide crystals such as ZnO***
- ***ammonia used instead of water; ammonia in a supercritical state (enhanced reactivity)***
- ***applied pressure and temperature: 1000-6000 atm. and 300–750^{o}C***
- ***mineralizers are added to the solution in order to increase the solubility of GaN feedstok***



acidic

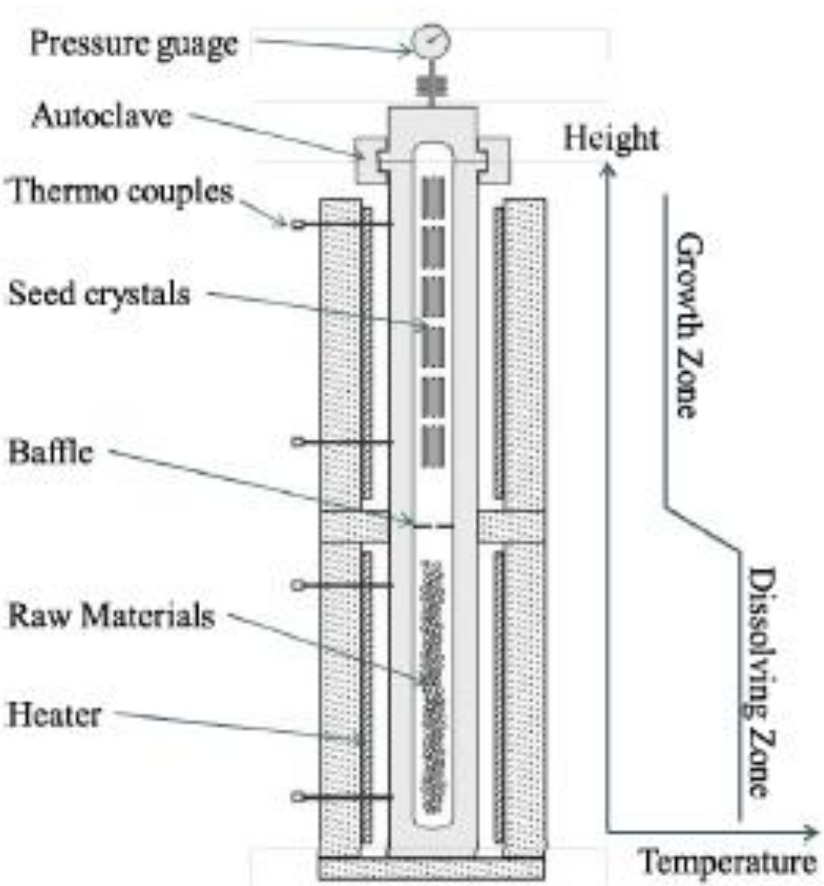


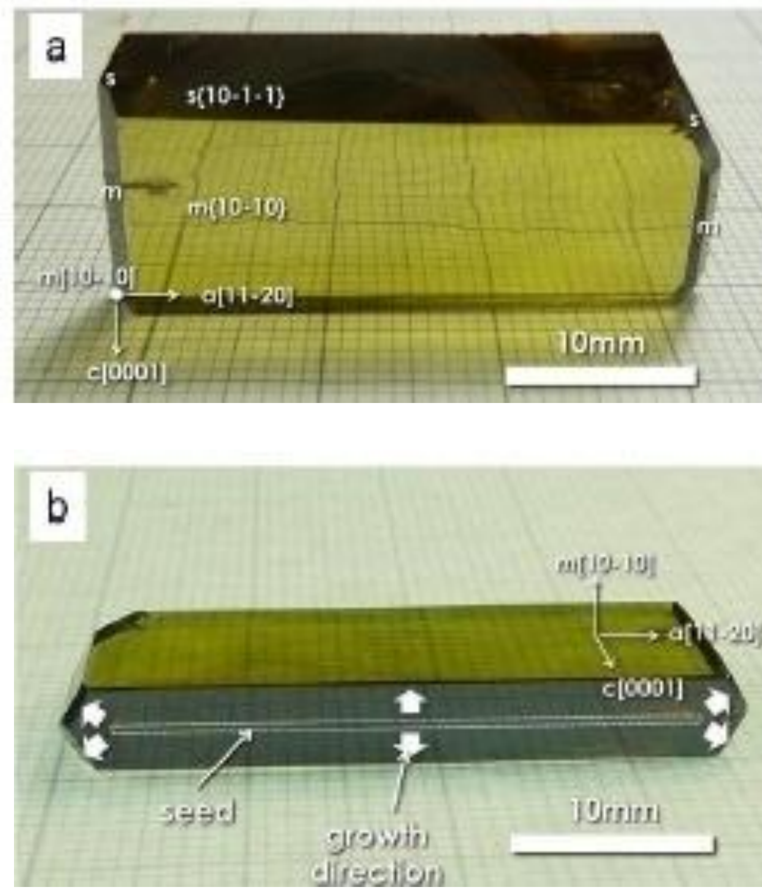
basic

Ammonothermal method SCAAT™

SuperCritical Acidic Ammonia Technology

MITSUBISHI CHEMICAL

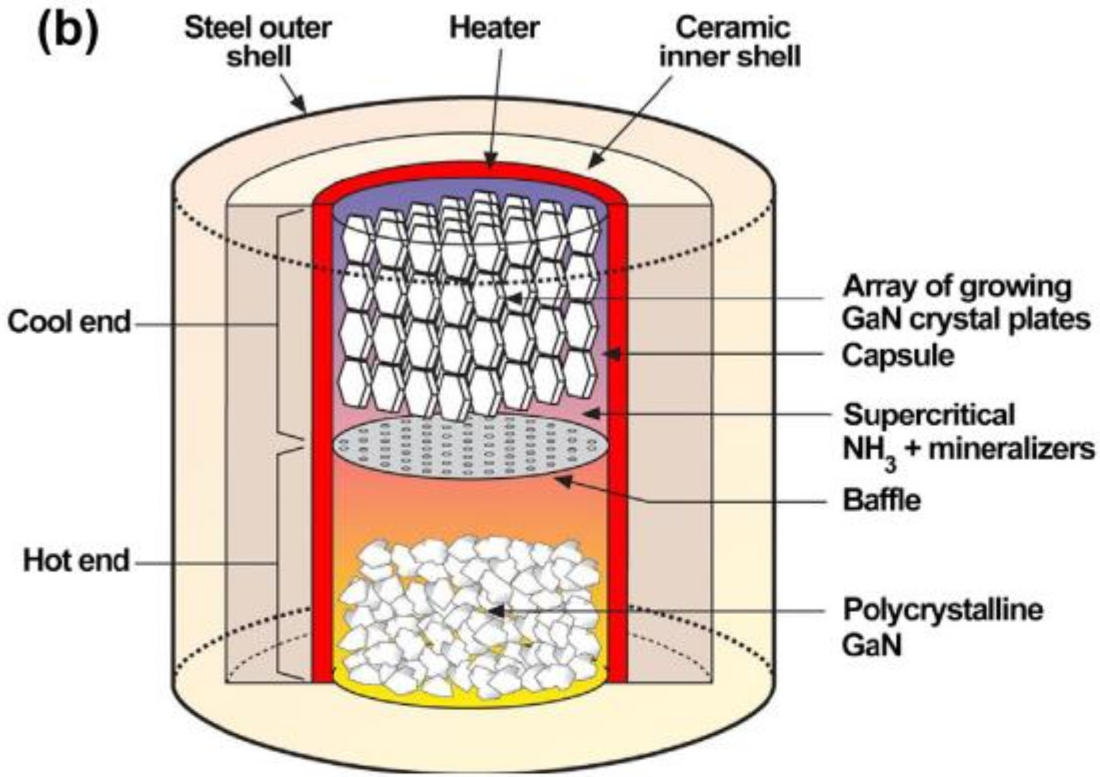


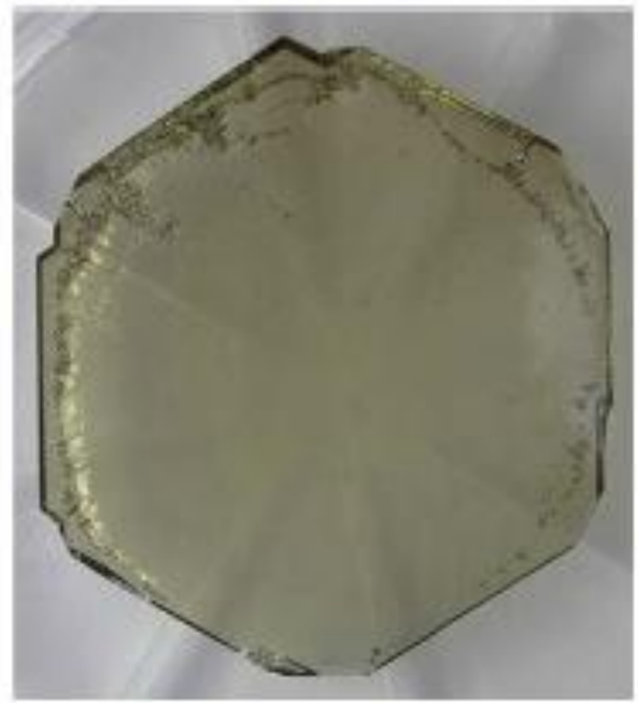


Y. Mikawa et al., Proc. of SPIE Vol. 9363, 936302 (2015)

Ammonothermal method SCoRA

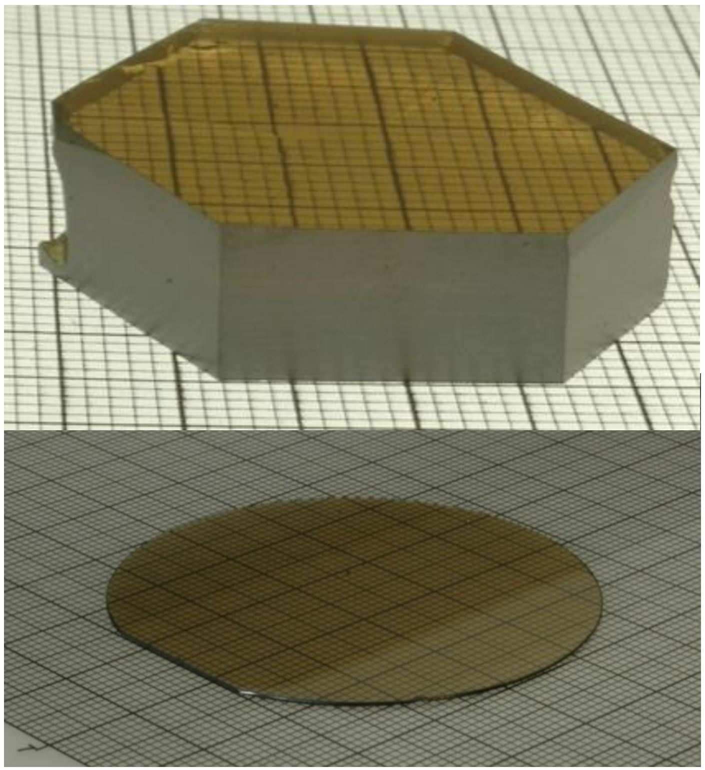
Scalable compact Rapid Ammonothermal technique from SORAA





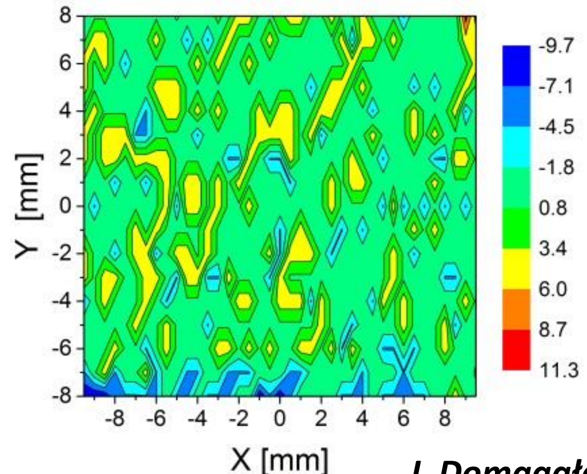
D. Ehrentraut and M. Bockowski, in Handbook of Crystal Growth Second Edition (2015)

Ammonothermal GaN from Ammono S.A.



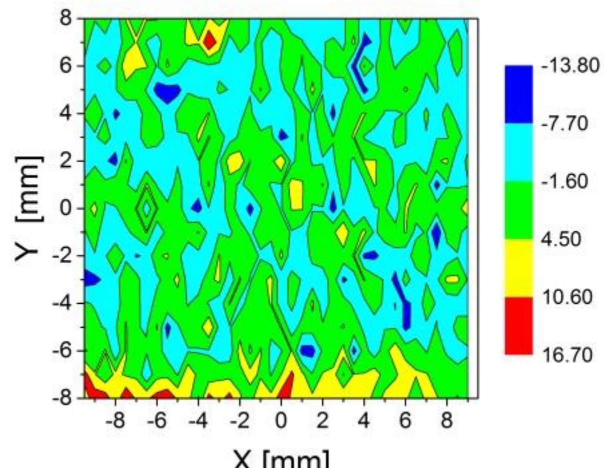
n-type ***($2x10^{17}$ to $2x10^{19}$ cm^{-3})***
semi-insulating ***(10^{6} -10^{10} Ωcm)***
p-type ***(10^{16} cm^{-3})***

<c>=5.18573±0.00003 Å



J. Domagała, IP PAS

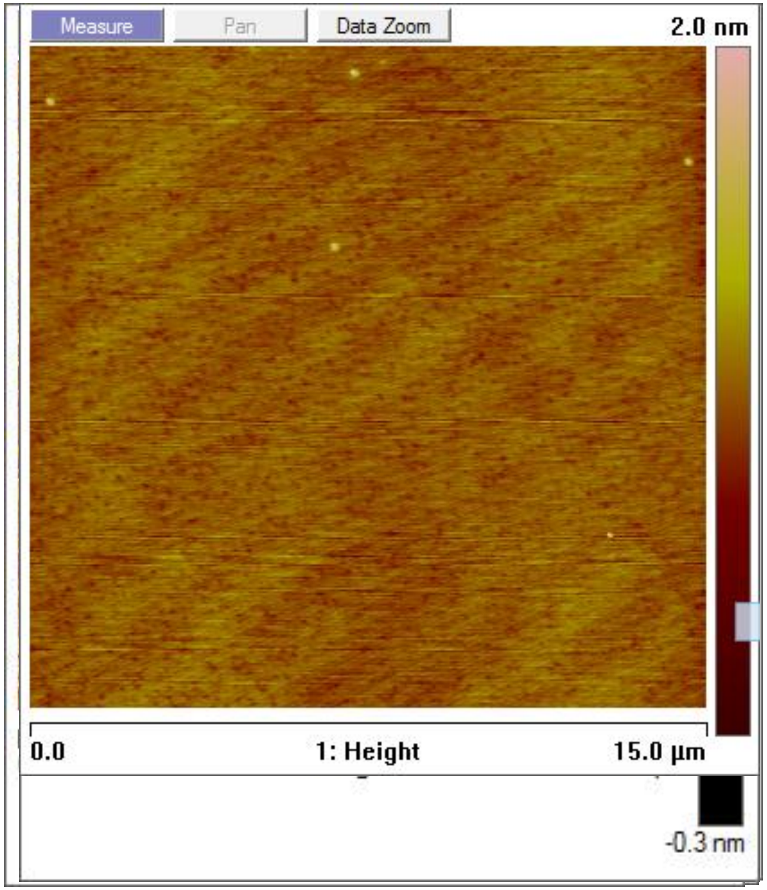
<a>=3.18930±0.00005 Å



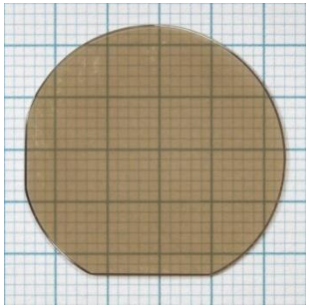
R. Doradziński et al. in Technology of Gallium Nitride Crystal Growth, Springer-Verlag, Heidelberg, 2010, pp. 137-158

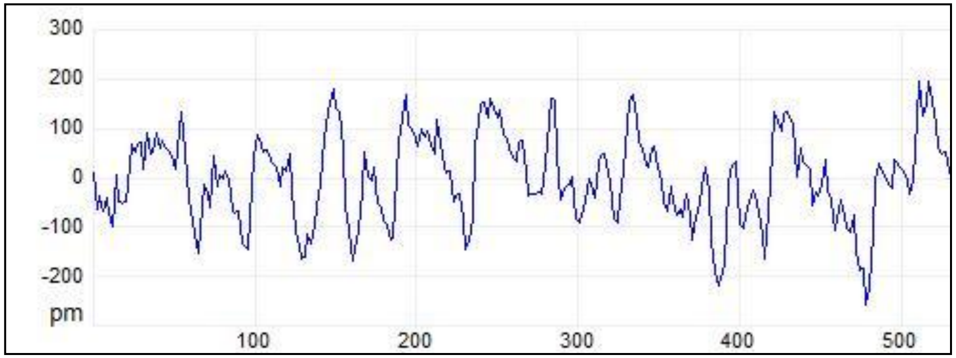
Ammonothermal GaN substrates

(0001) surface preparation



CMP + cleaning





RMS < 0.1 nm

Visible atomic steps

A. Sidor, G. Nowak, G. Kamler, A. Pawłowska, A. Nowakowska-Siwińska

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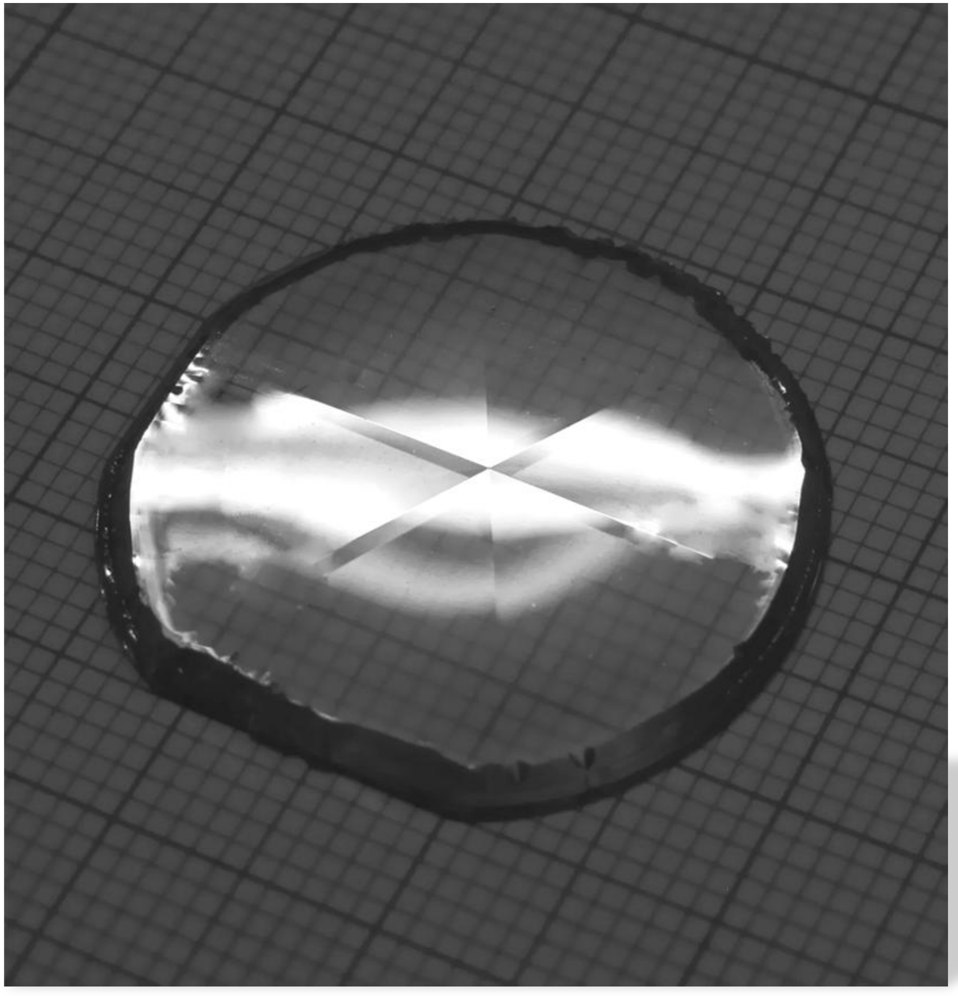
HVPE growth on Ammono-GaN



Japanese Journal of Applied Physics 55, 05FC01 (2016)

High-quality, 2-inch-diameter *m*-plane GaN substrates grown by hydride vapor phase epitaxy on acidic ammonothermal seeds

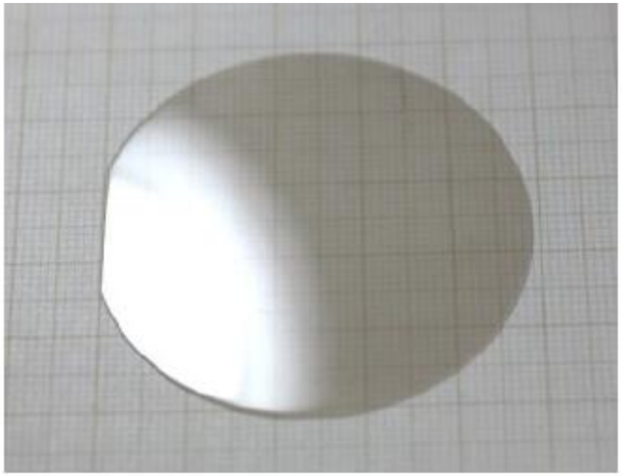
Yusuke Tsukada[1*], Yuuki Enatsu[1], Shuichi Kubo[1], Hirotaka Ikeda[1], Kaori Kurihara[1], Hajime Matsumoto[2], Satoru Nagao[2], Yutaka Mikawa[1], and Kenji Fujito[1]

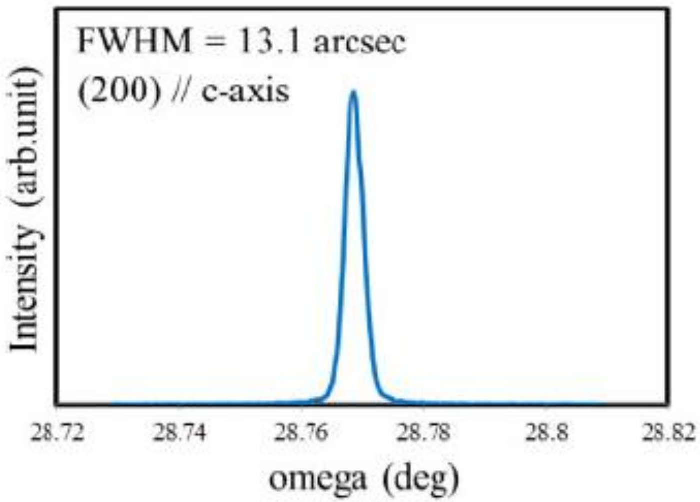
[1]*R&TD Center, Tsukuba Plant, LED Materials Department, Mitsubishi Chemical Corporation, Ushiku, Ibaraki 300-1295, Japan*
[2]*MCHC R&D Synergy Center Inc., Yokohama 227-8502, Japan*

*E-mail: 3619242@cc.m-kagaku.co.jp

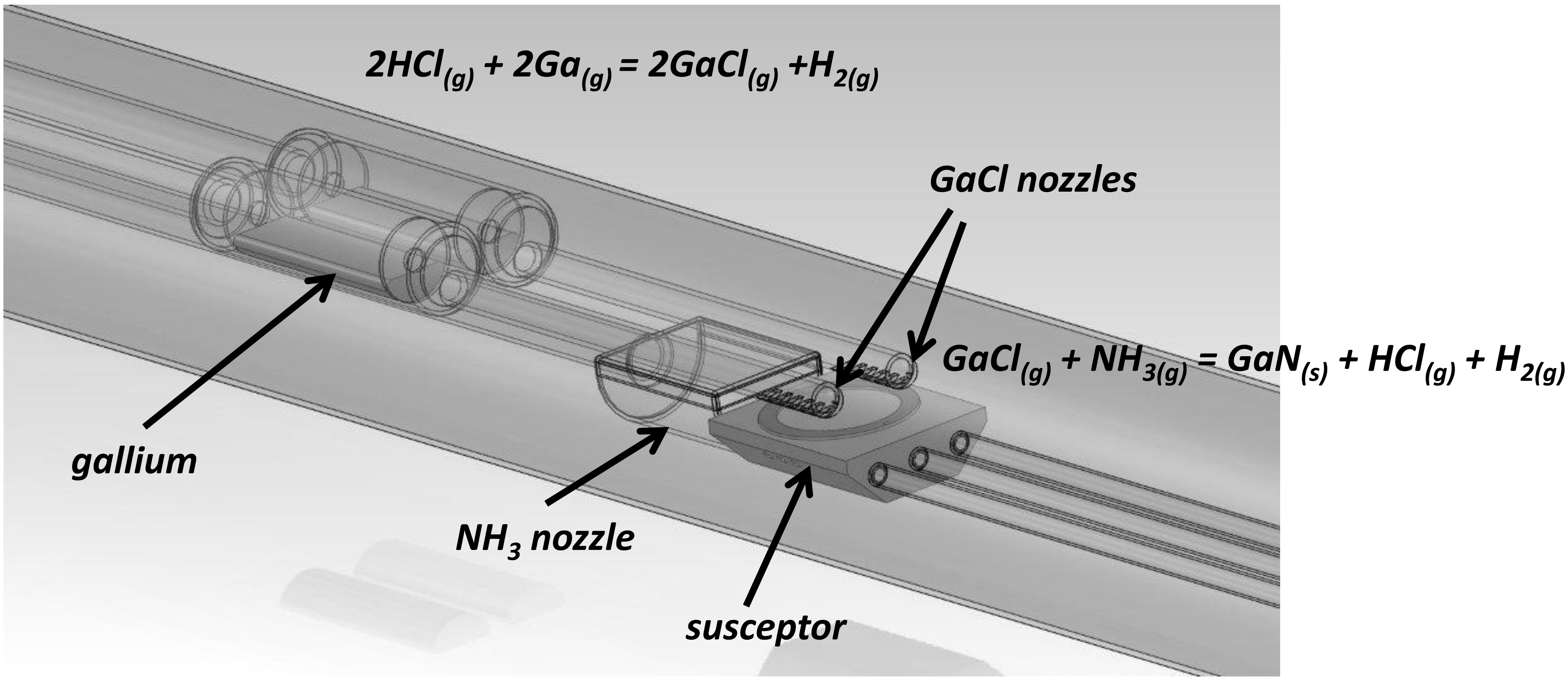
Received November 5, 2015; revised November 17, 2015; accepted November 19, 2015; published online March 1, 2016

In this paper, we discusse the origin of basal-plane stacking faults (BSFs) generated in the homoepitaxial hydride vapor phase epitaxy (HVPE) growth of *m*-plane gallium nitride (GaN). We investigated the effects of seed quality, especially dislocation density, on BSF generation during homoepitaxy. The results clearly identify basal-plane dislocation in the seed as a cause of BSF generation. We realized high-quality *m*-plane GaN substrates with a 2-in. diameter using HVPE on low-dislocation-density *m*-plane seeds.





Our HVPE reactor configuration



T. Sochacki et al. Journal of Crystal Growth 407 (2014) 52–57

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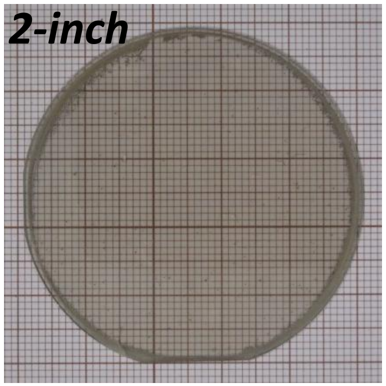
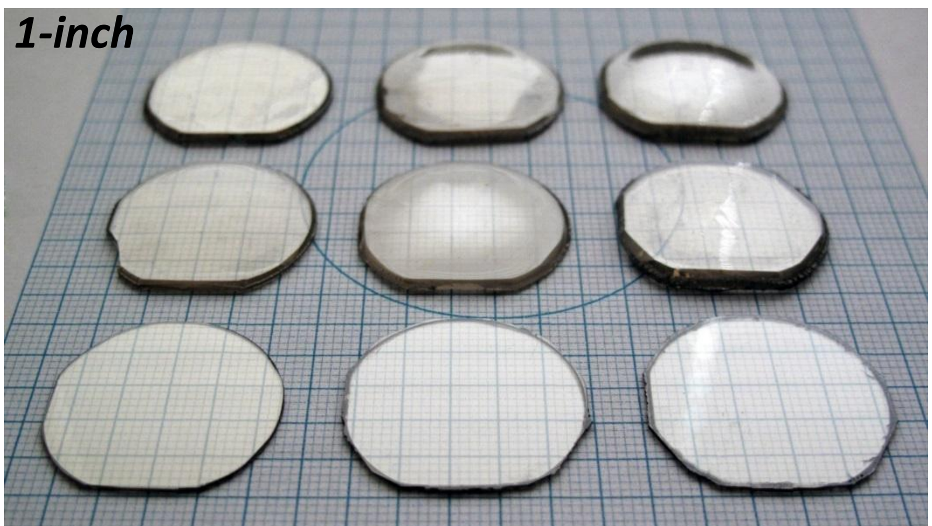
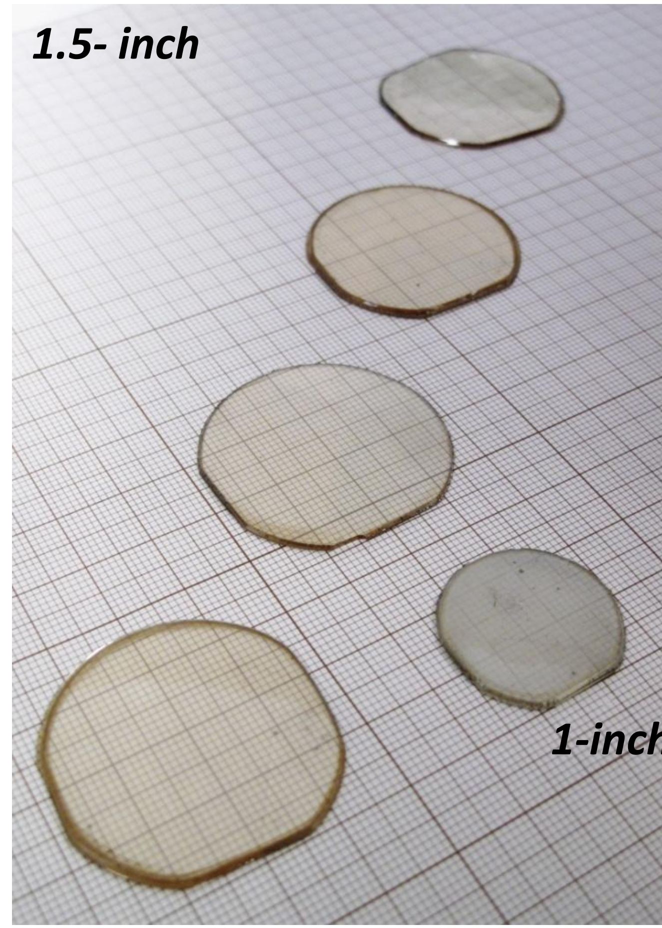
HVPE-GaN layers on Ammono-GaN seeds



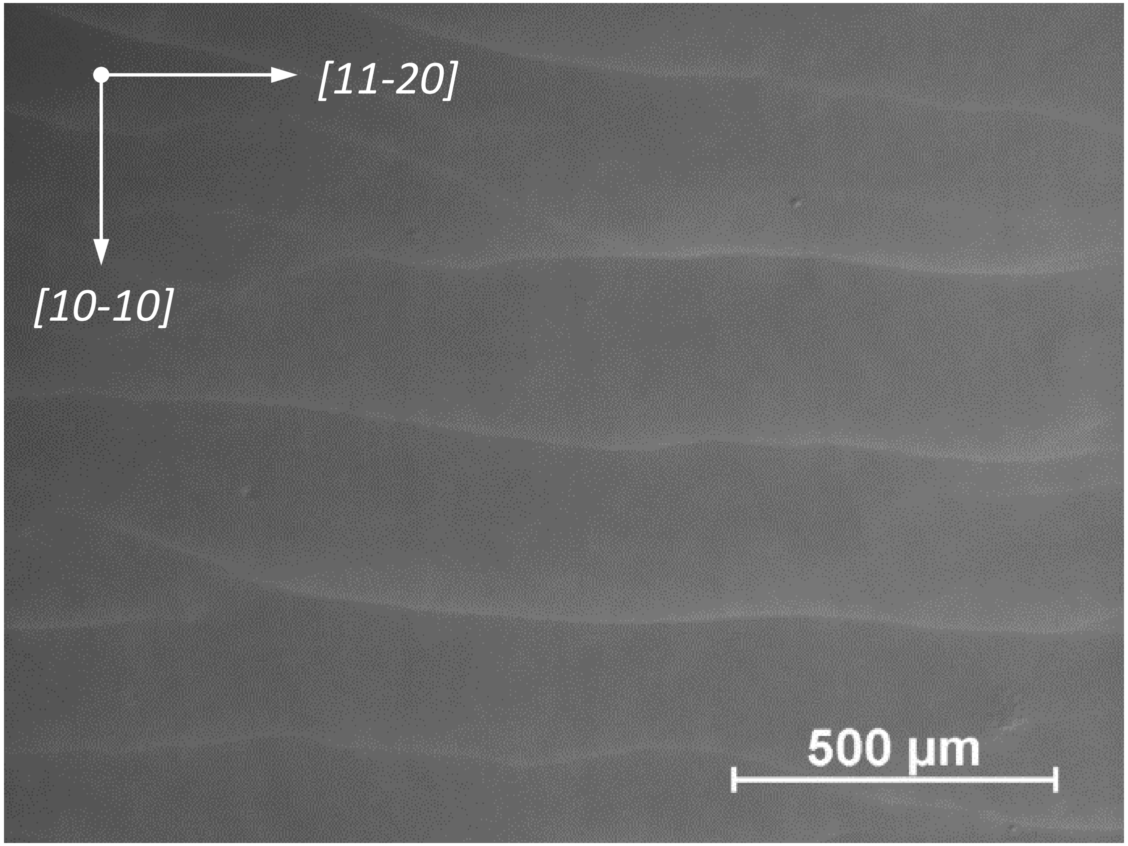




B. Łucznik, T. Sochacki, M. Amilusik, M. Fijałkowski, M. Iwińska, P. Kempisty, I. Grzegory

HVPE growth modes: macrosteps

After 1-2 h. of growth



Average growth rate: 60-80 µm/h

T. Sochacki et al. Journal of Crystal Growth 403 (2014) 32–37

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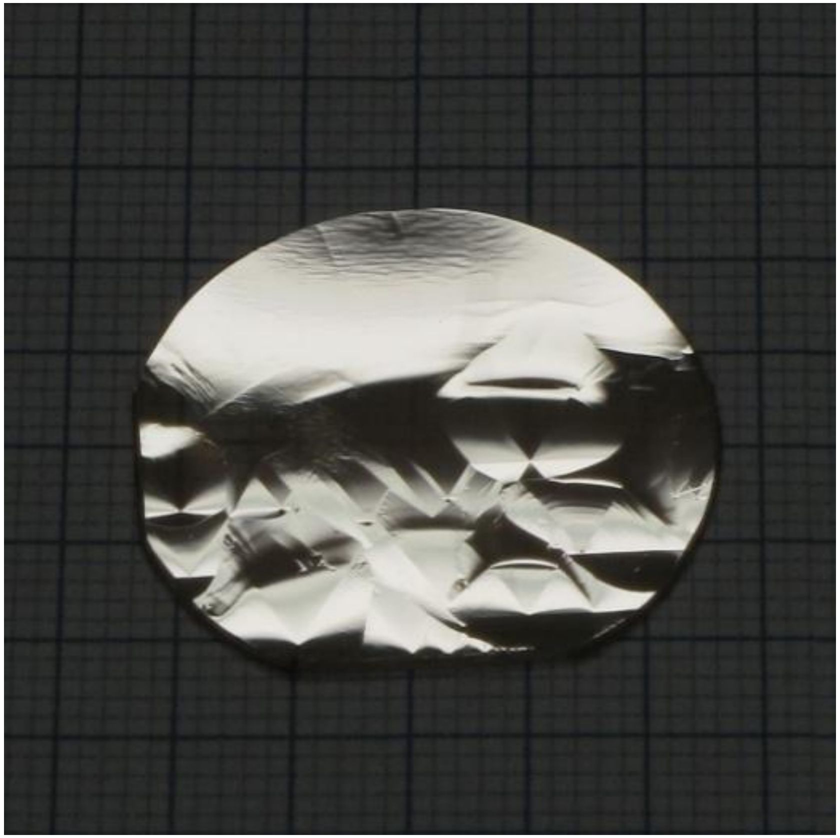
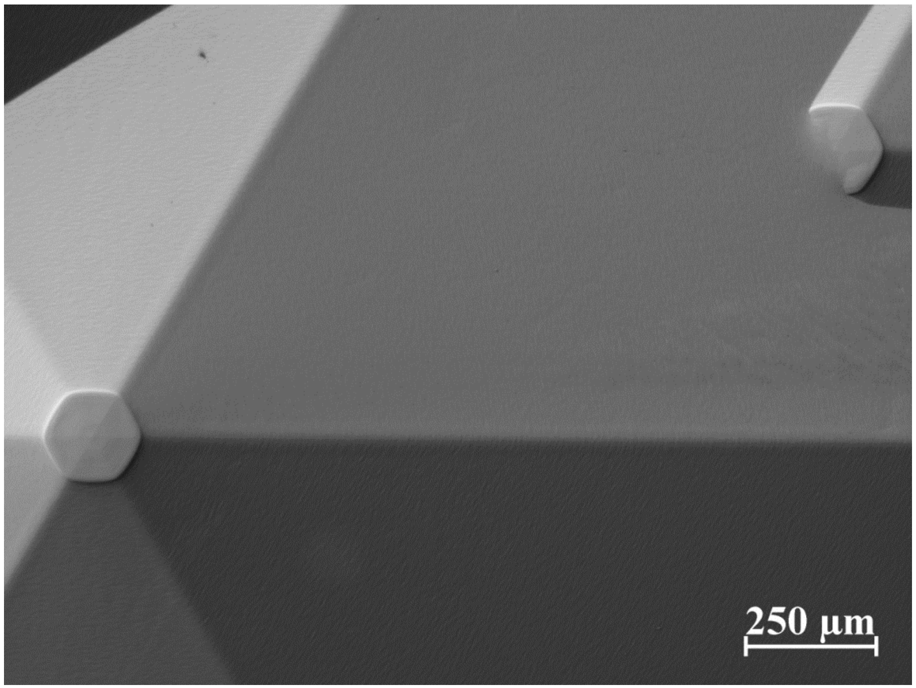
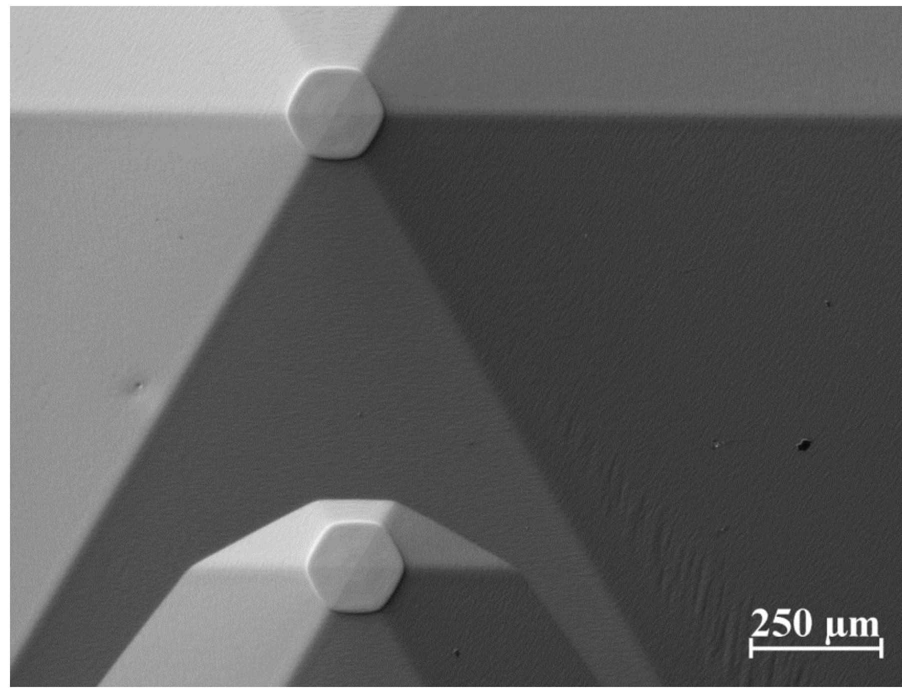
HVPE growth modes: hillocks and steps



HVPE growth modes: hillocks





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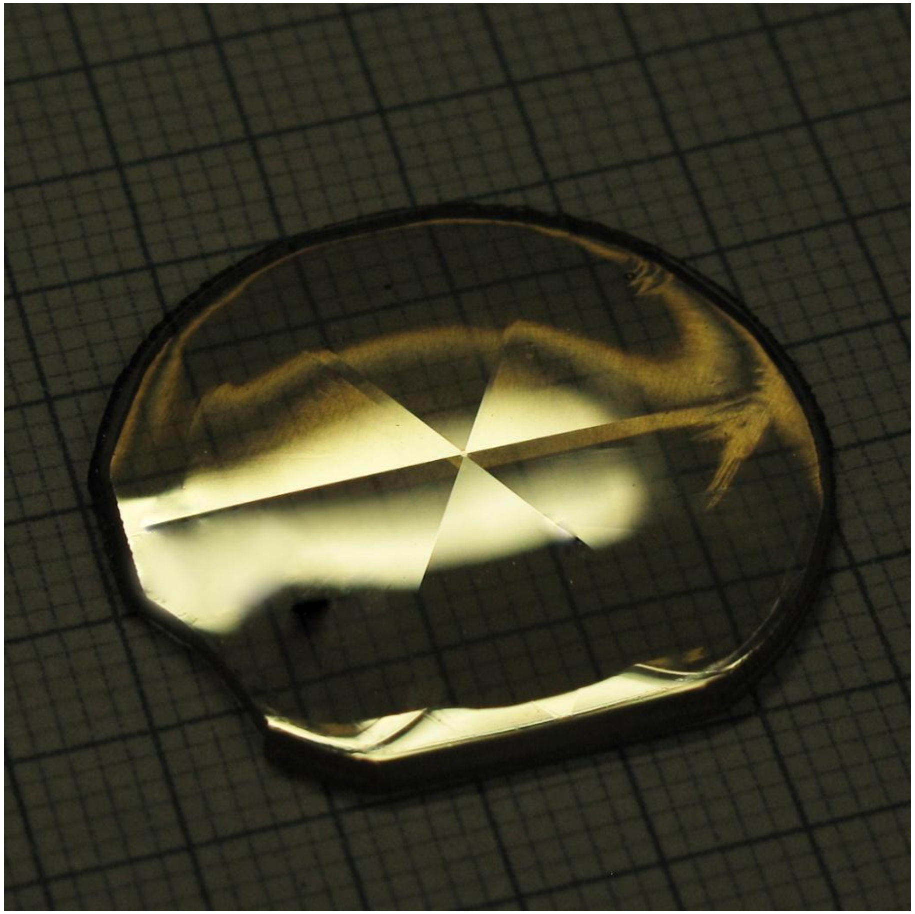
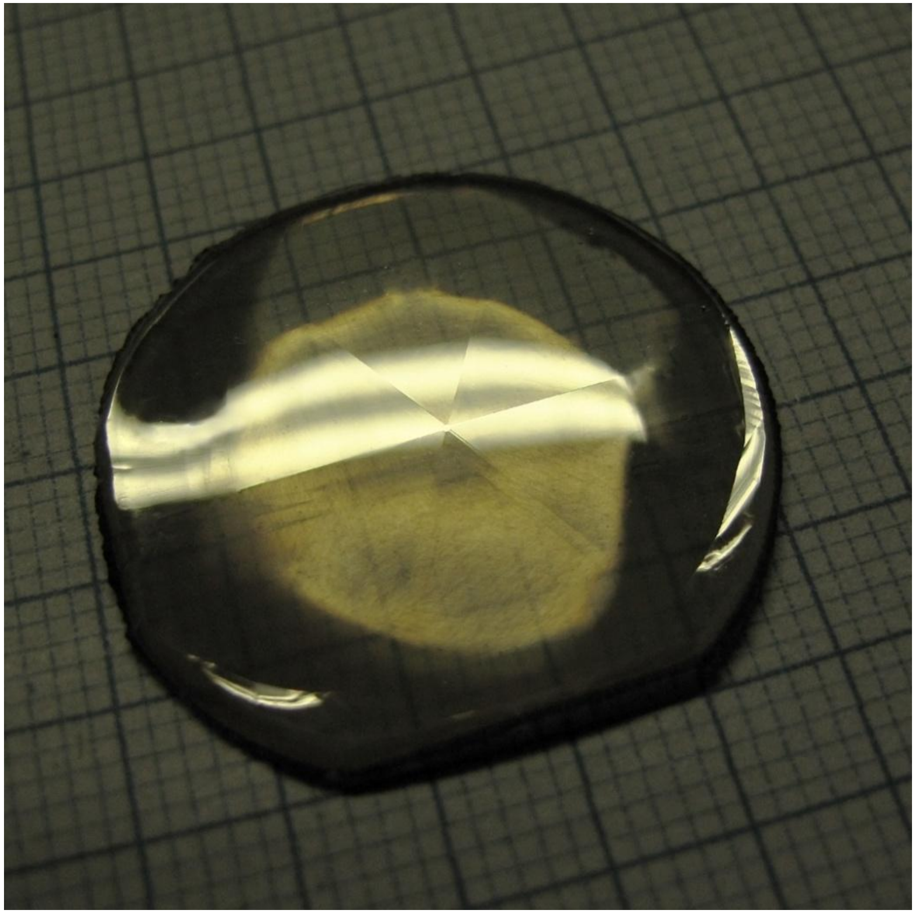
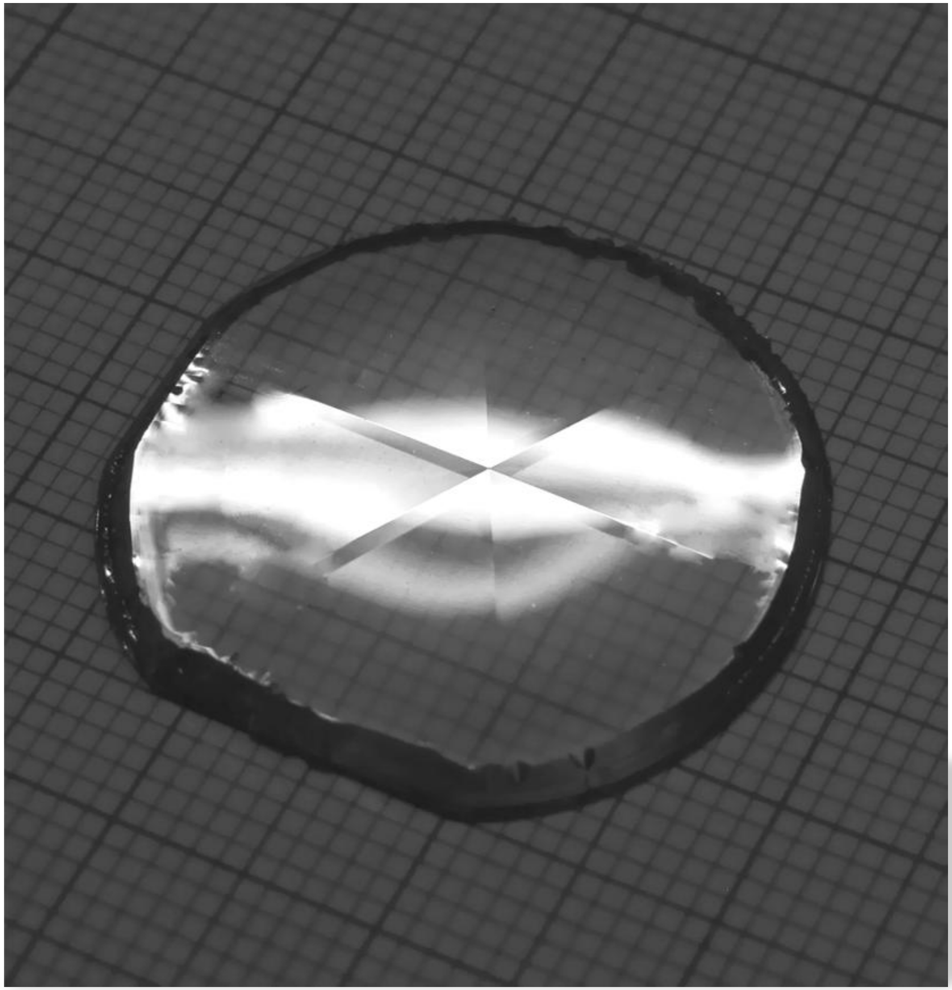
HVPE growth modes: hillocks





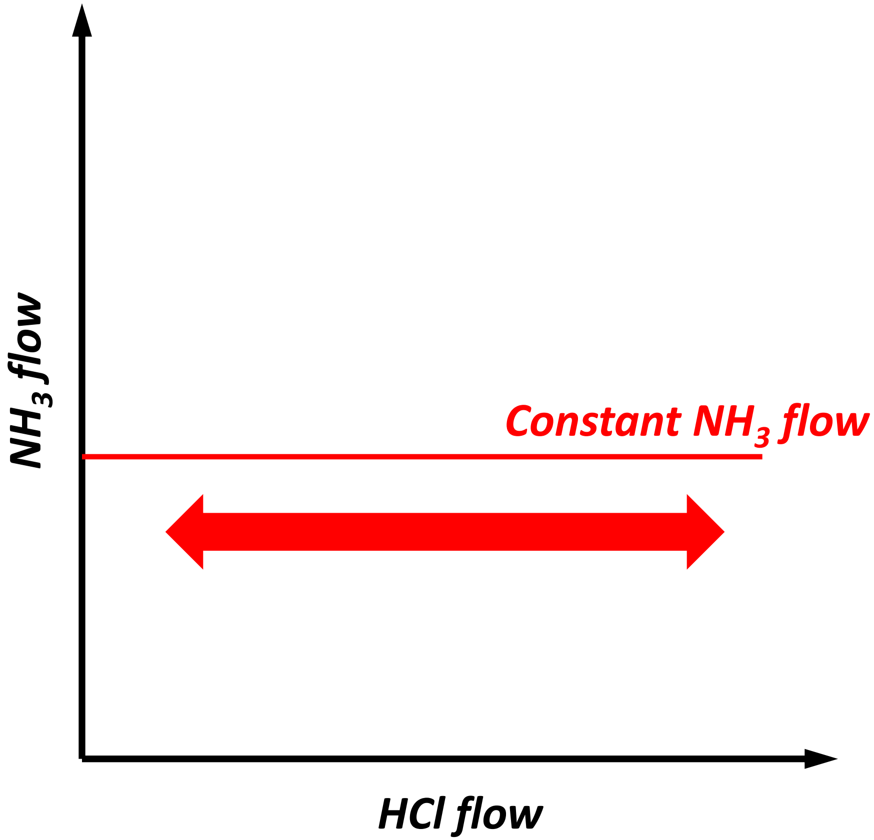
Average growth rate: 150-380 μm/h
in 10 – 2 hrs.

Growth rate



Growth rate

$$2Ga_{(l)} + 2HCl_{(g)} = 2GaCl_{(g)} + H_{2(g)}$$
$$GaCl_{(g)} + NH_{3(g)} = GaN_{(s)} + HCl_{(g)} + H_{2(g)}$$



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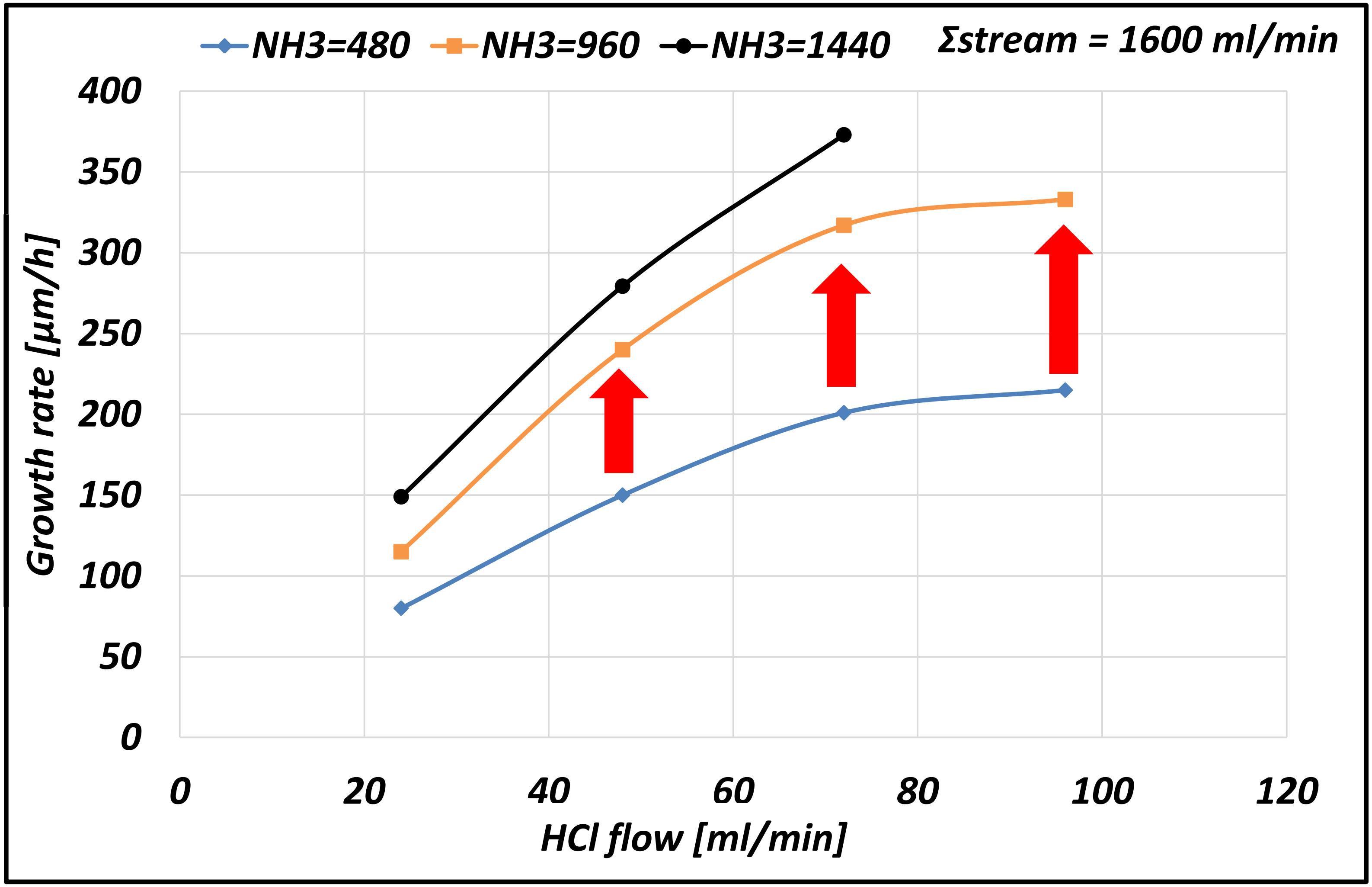
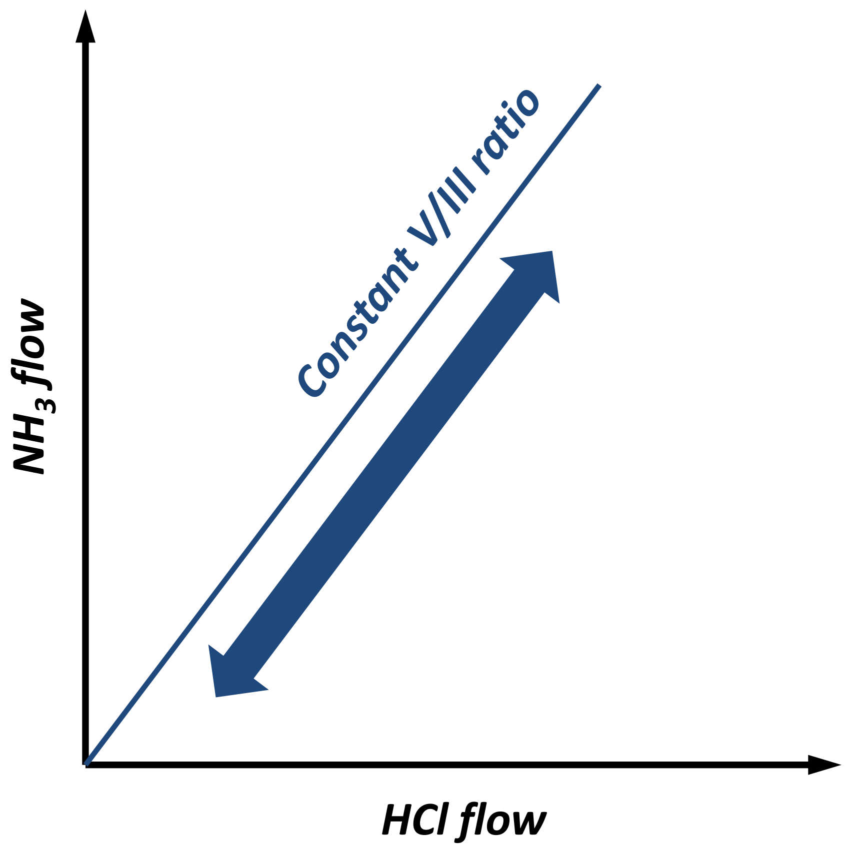
Growth rate



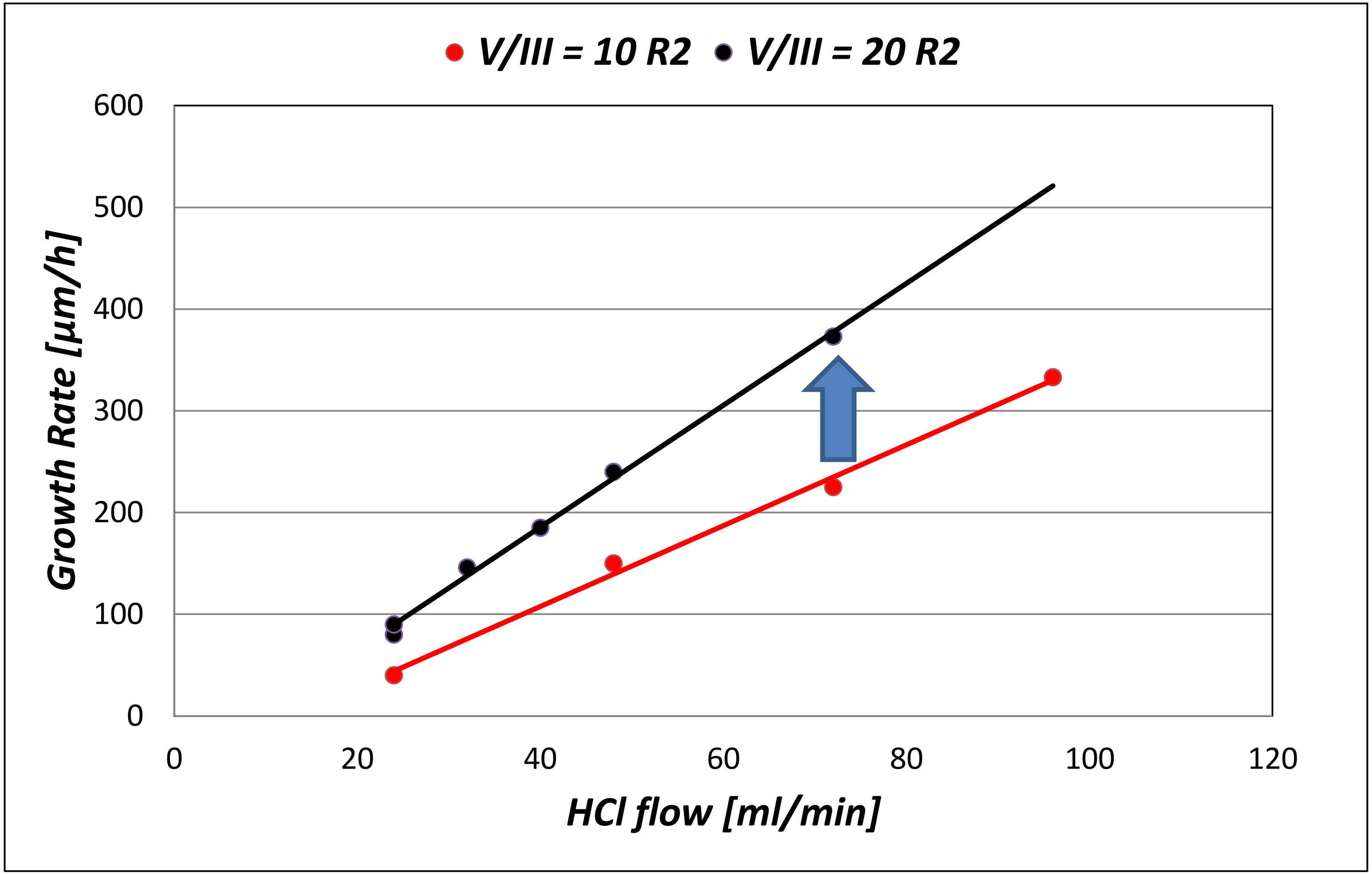
Growth time 8 h.

Growth rate

$$2Ga_{(l)} + 2HCl_{(g)} = 2GaCl_{(g)} + H_{2(g)}$$
$$GaCl_{(g)} + NH_{3(g)} = GaN_{(s)} + HCl_{(g)} + H_{2(g)}$$

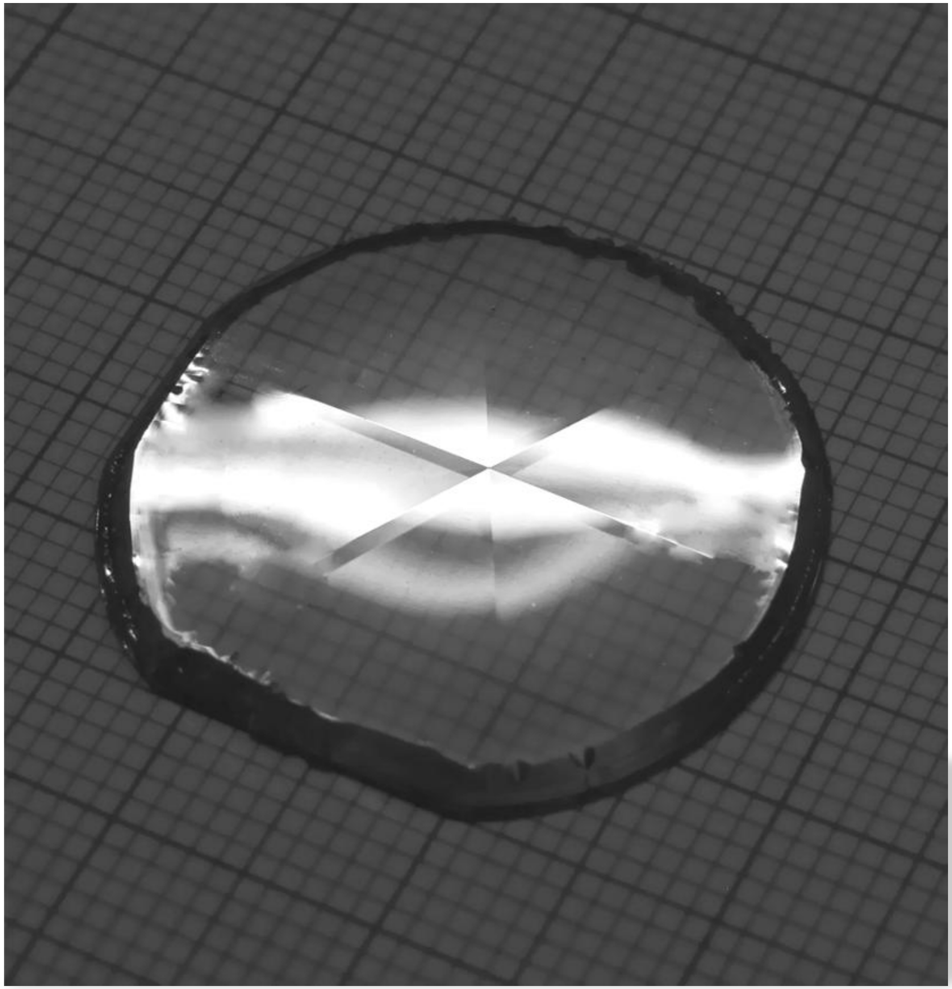


Growth rate

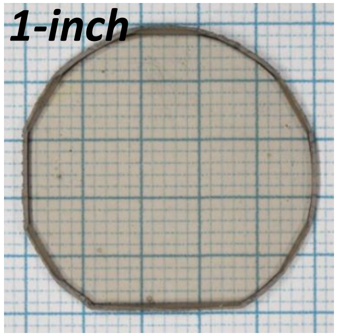


Growth time 8 h.

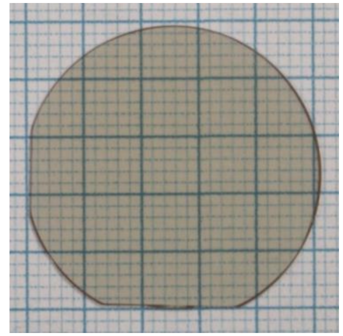
Wafering

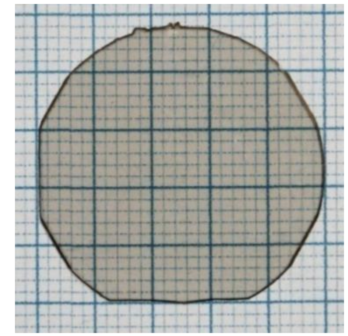


Slicing of HVPE-GaN/Am-GaN



Slicing

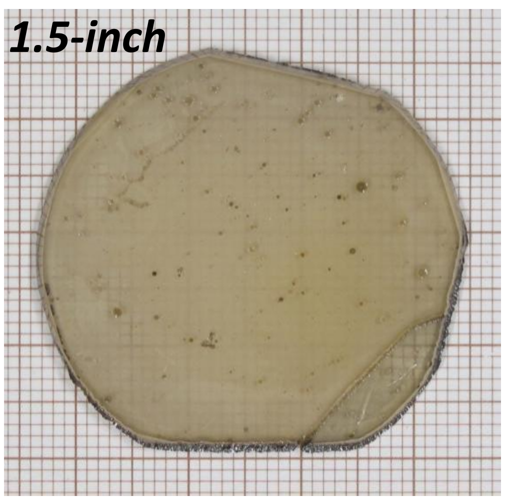




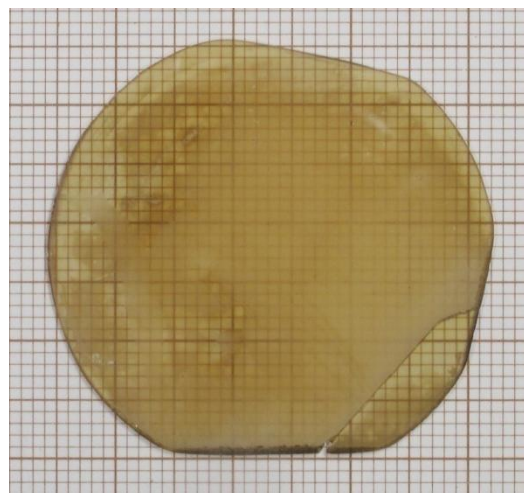
HVPE-GaN/Am-GaN

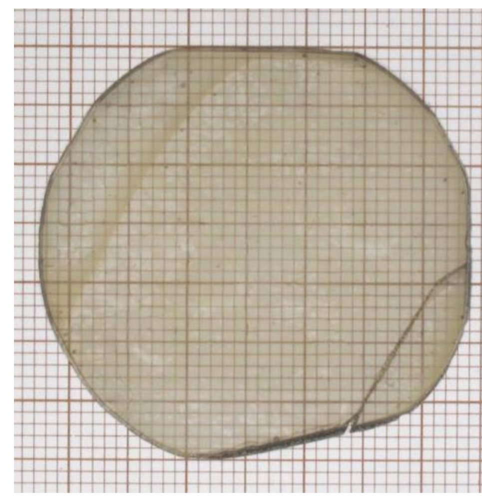
HVPE-GaN/Am-GaN

F-S HVPE-GaN



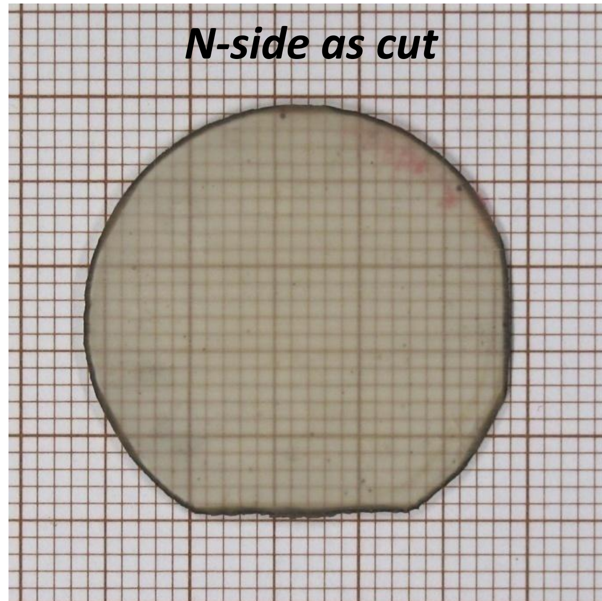
Slicing

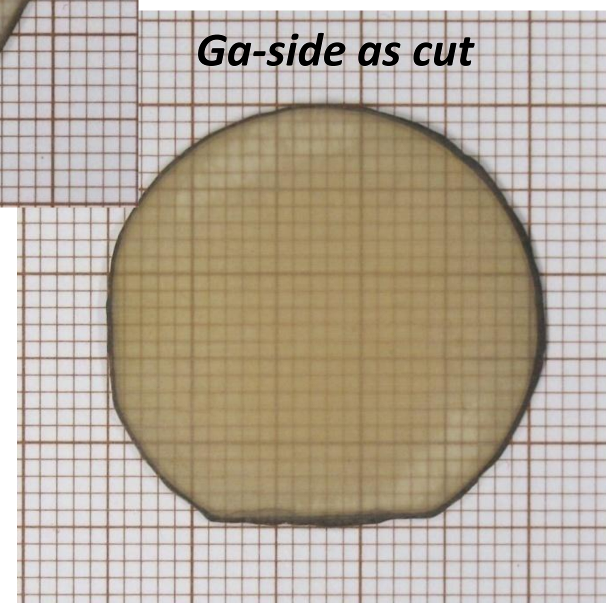




Slicing of HVPE-GaN/Am-GaN

WSD-K2 Single Wire Saw

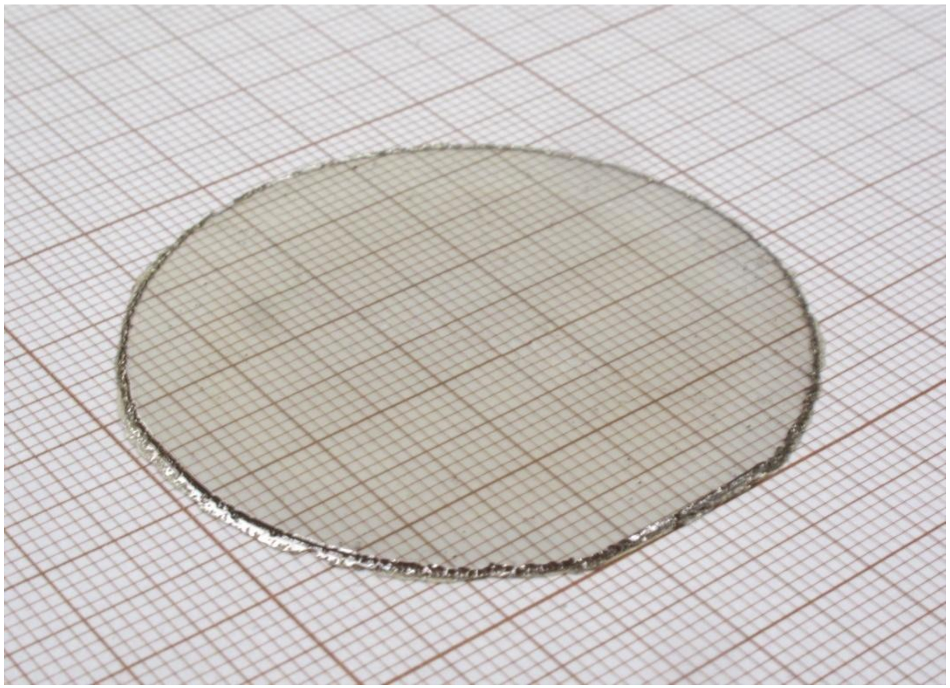


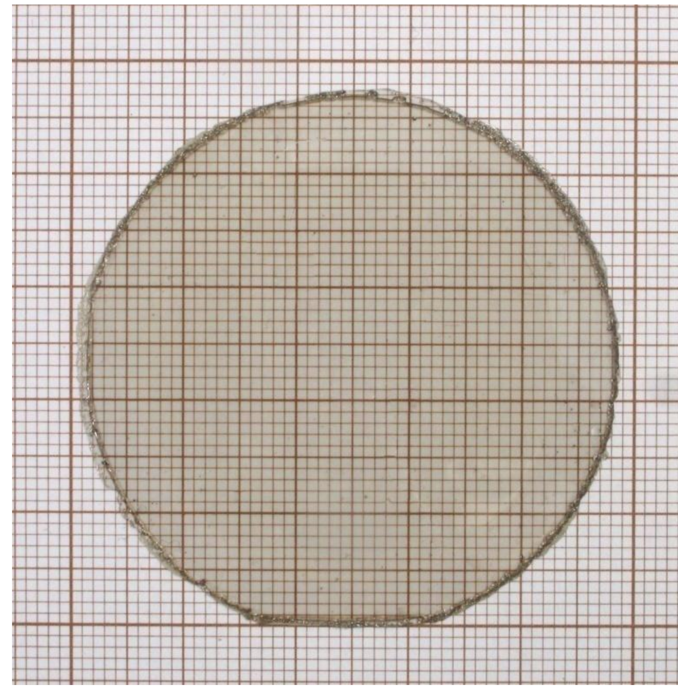


1-inch
Slicing time: 2.5 h.
Bow < 10 µm
TTV = 20 µm

T. Sochacki

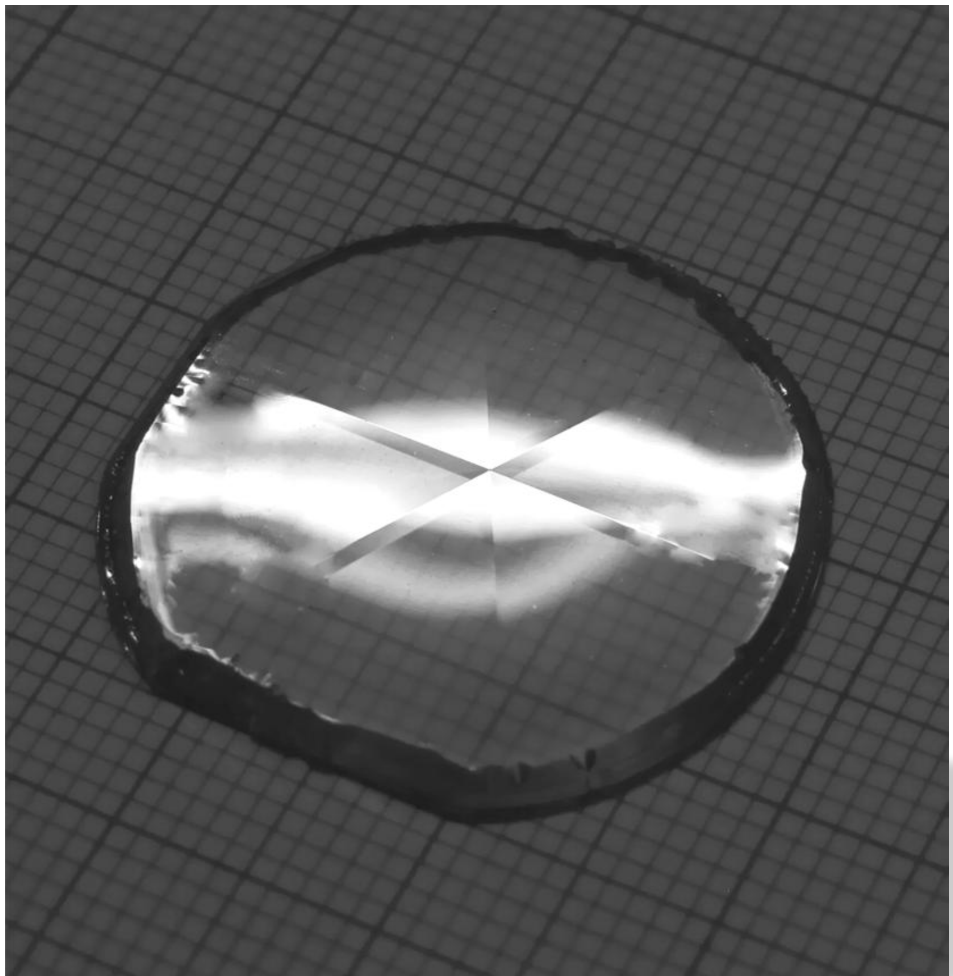
2-inch F-S HVPE-GaN





R = 100 μm/h
Thickness = 500 μm
EPD = $5x10^{4}$ cm^{-2}
n = ~10^{17} cm^{-3}

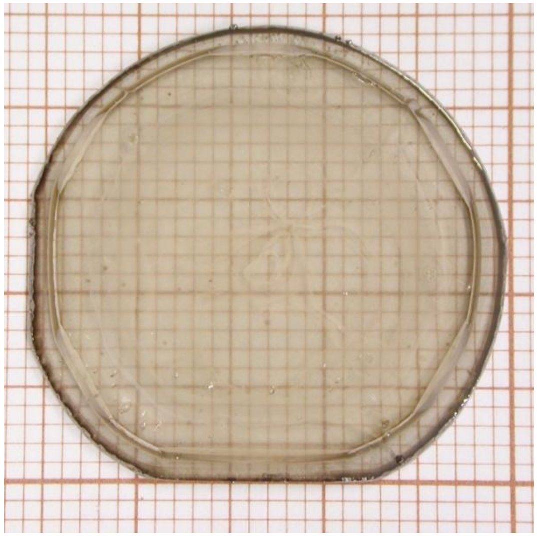
Regrowth by HVPE and ammonothermal methods



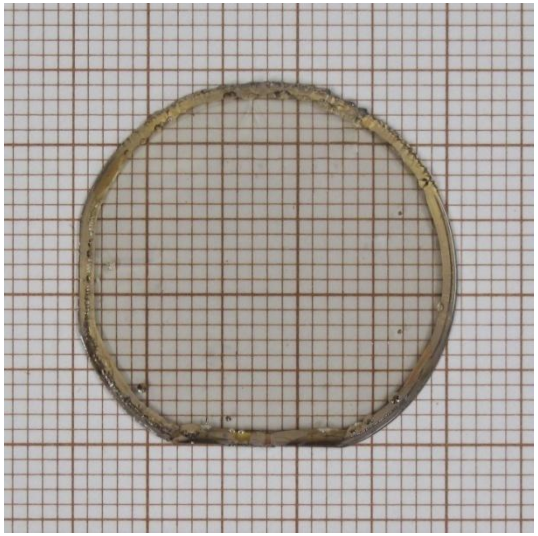
Regrowth by HVPE method

Three crystals after third re-growth procedure

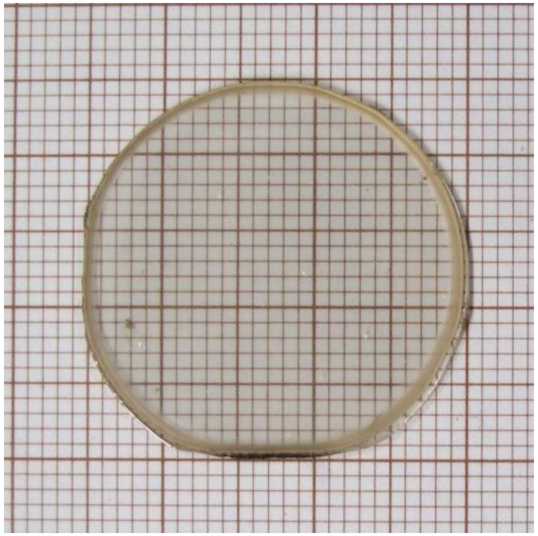
Crystal no. 3



Crystal no. 2



Crystal no. 1



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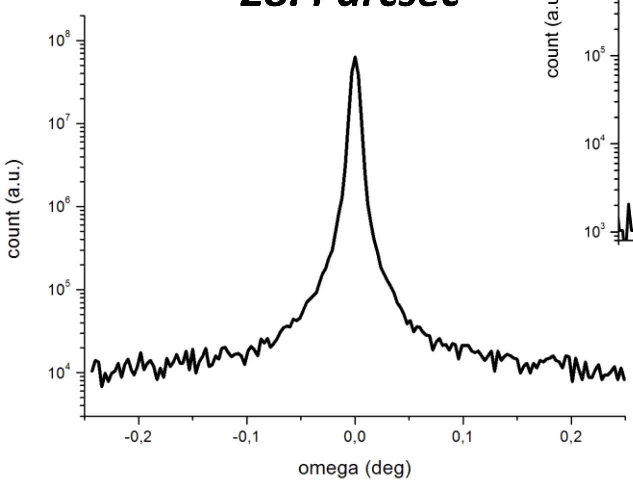
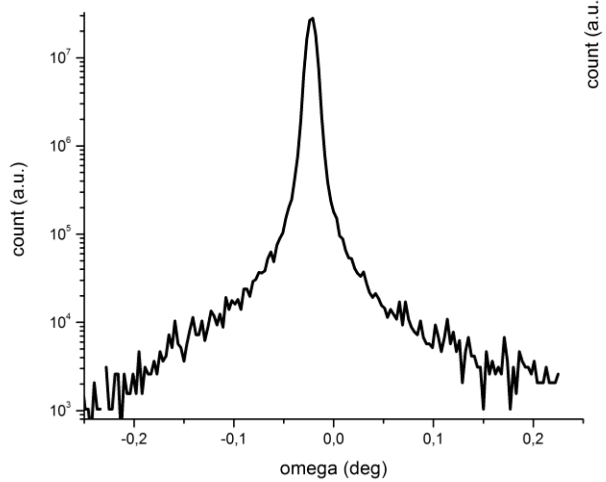
Regrowth by HVPE method

X-ray rocking curve for as-grown HVPE-GaN crystals after three re-growth procedures

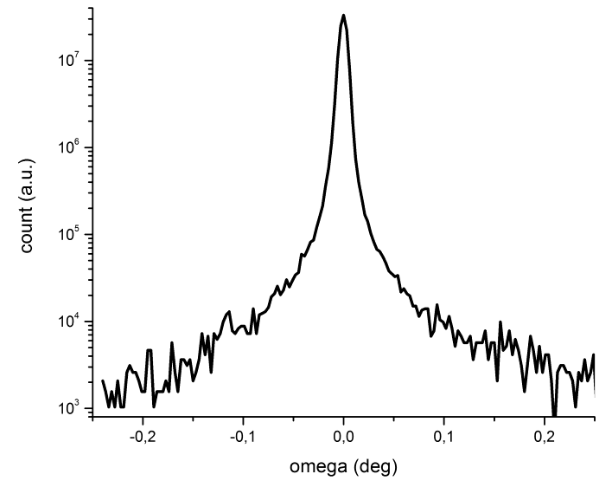
Crystal no. 1
FWHM (002)
28.4 arcsec



Crystal no. 2
FWHM (002)
38.2 arcsec

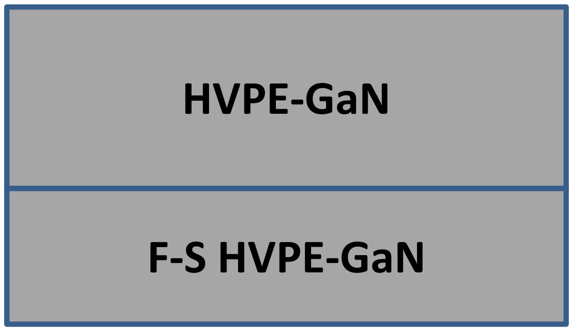


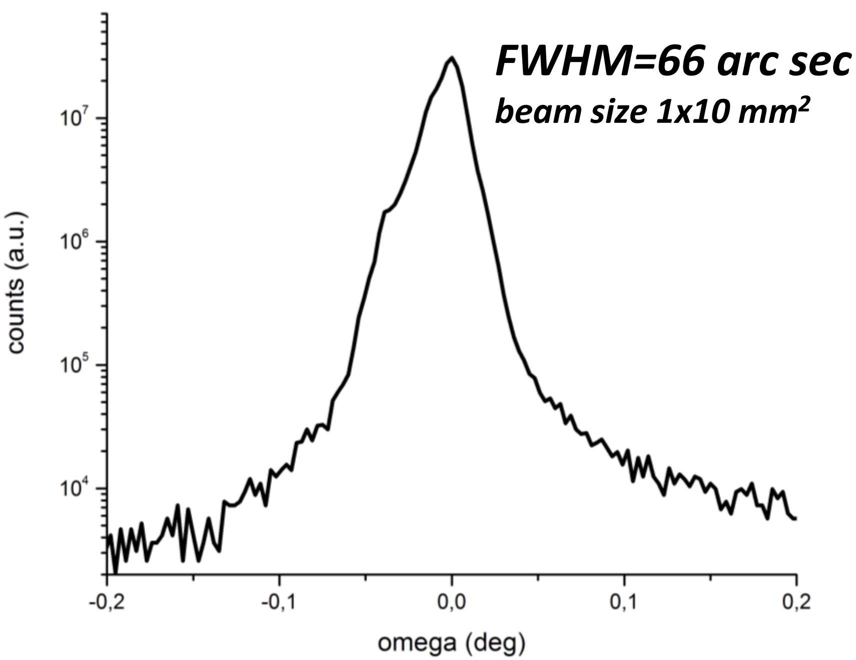
Crystal no. 3
FWHM (002)
32.4 arcsec

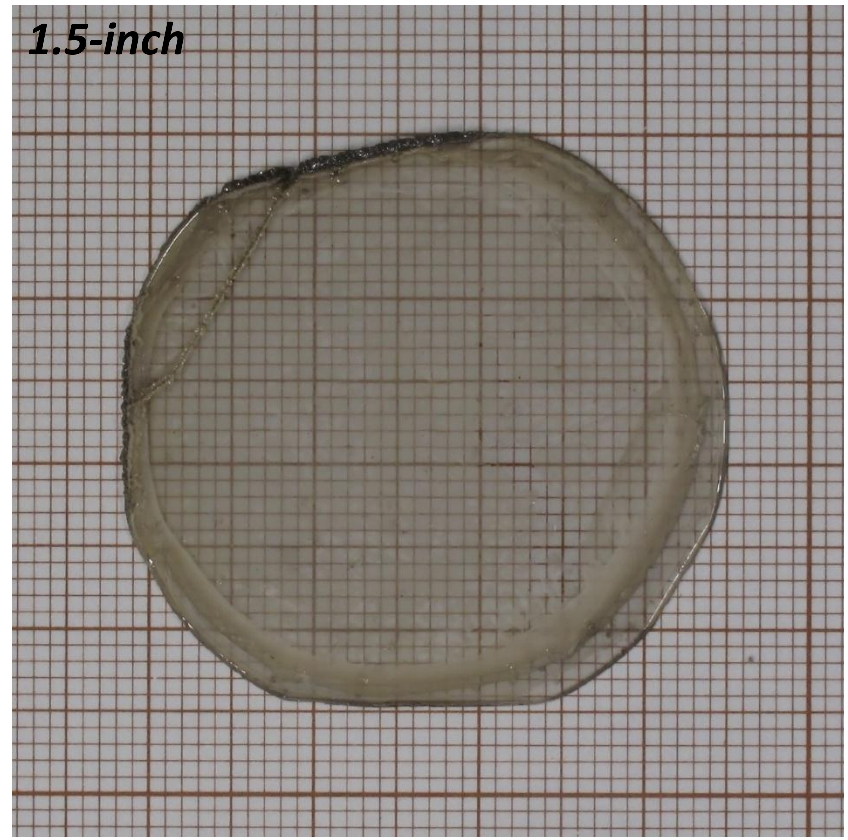


beam size 1x10 mm^2

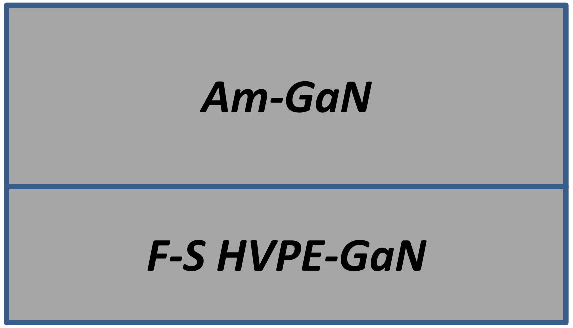
Regrowth by HVPE method

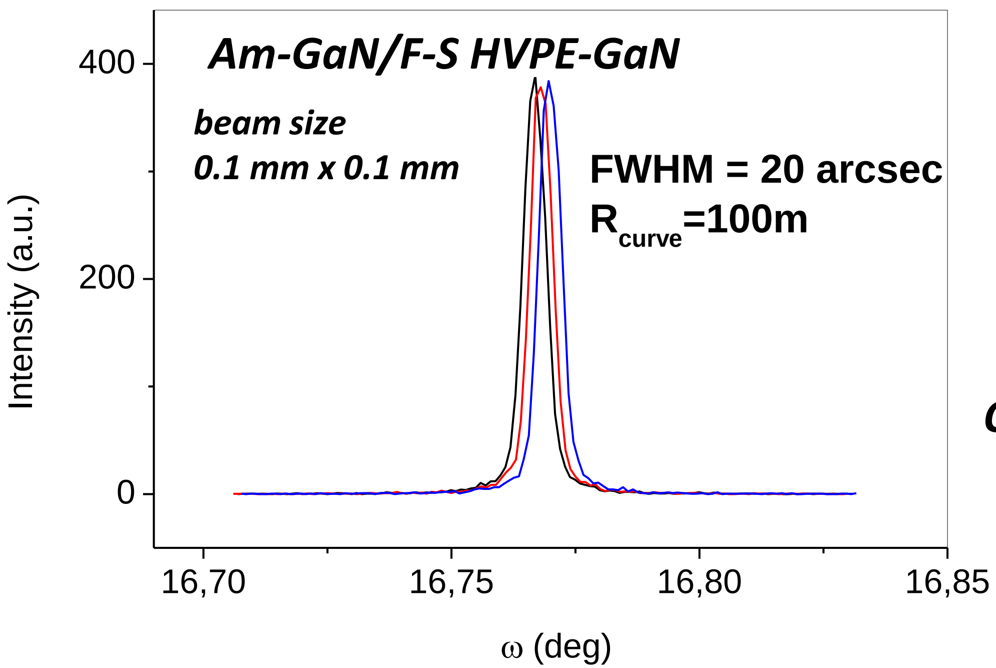


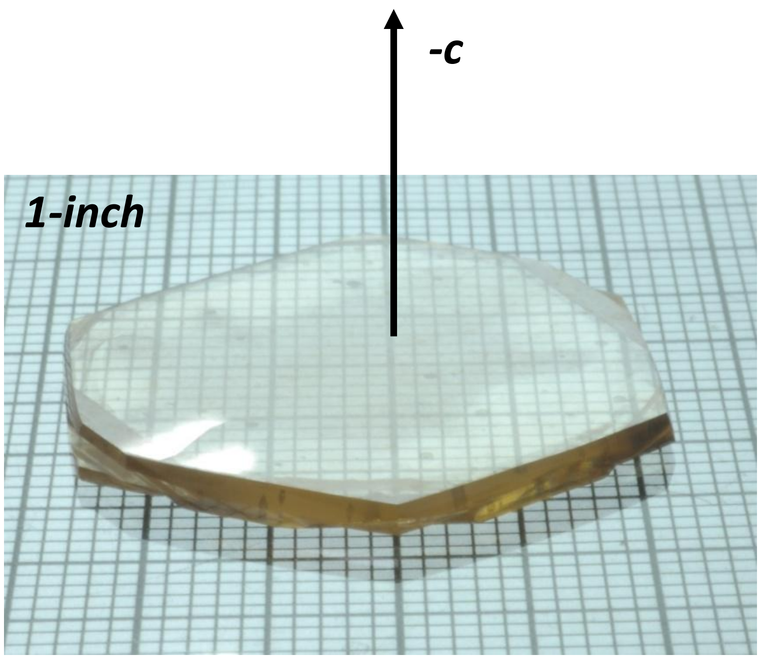




Regrowth by ammonothermal method







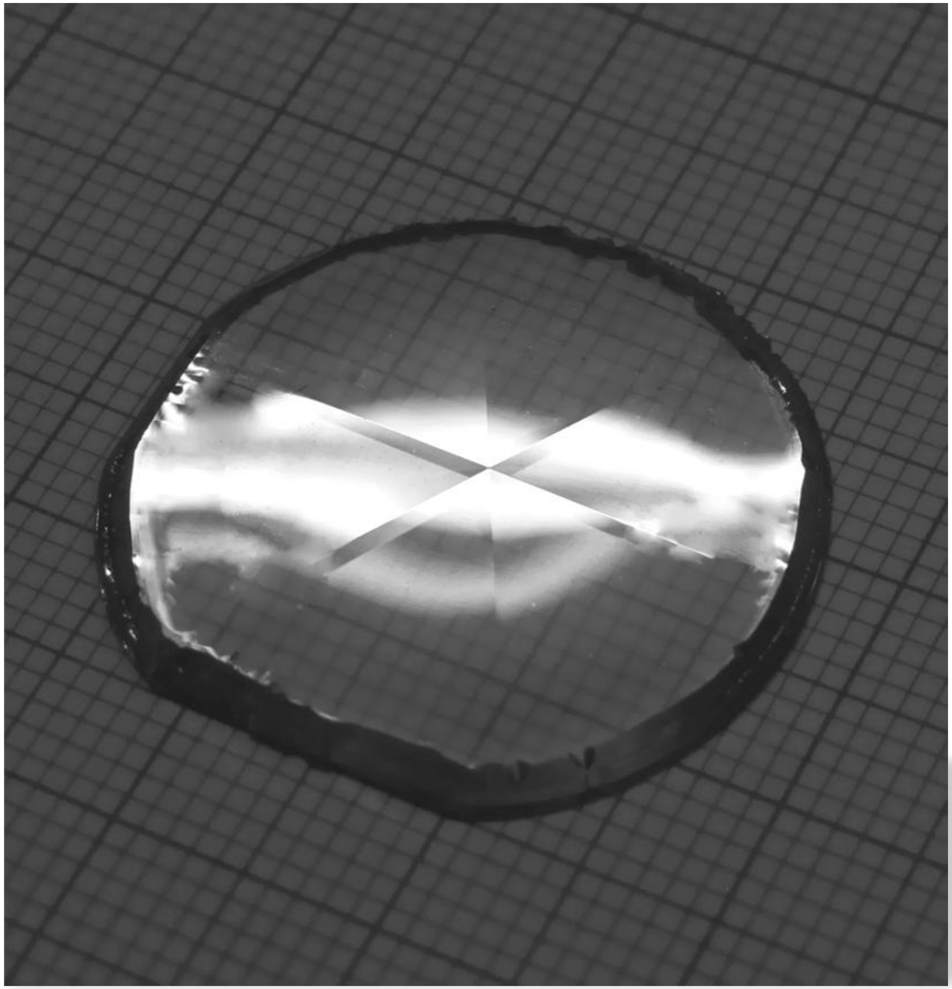
Conductivity: n-type (n~ $5x10^{17}$ cm^{-3})

Oxygen concentration (SIMS) – $1x10^{18}$ cm^{-3}

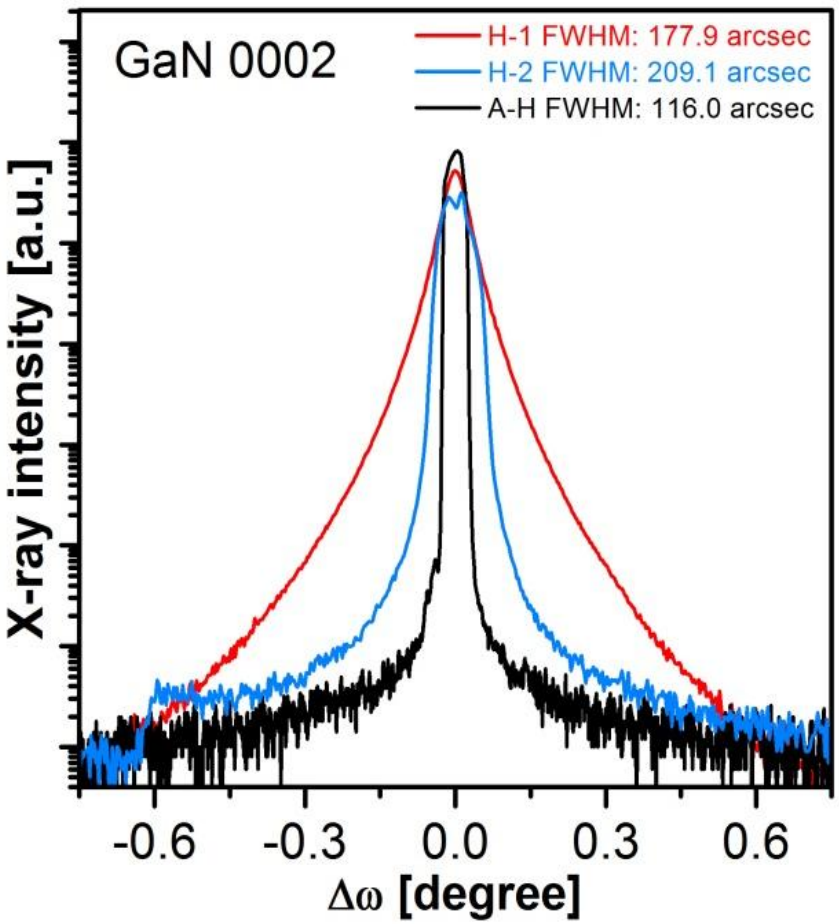
Absorption coefficient ~ 3 cm^{-1} at 450 nm

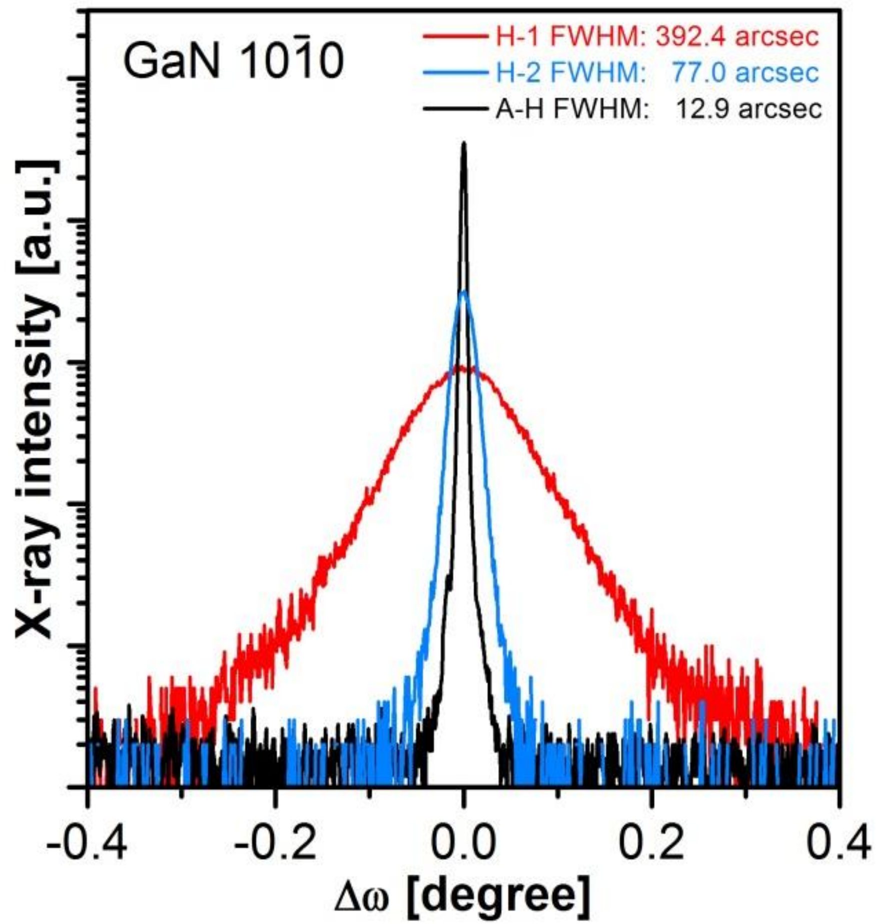
R. Kucharski et al. Journal of Crystal Growth 427 (2015) 1–6

Properties of F-S HVPE-GaN



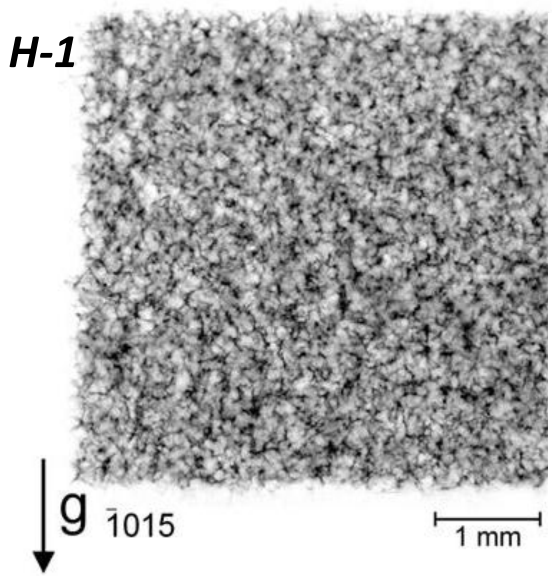
Structural quality of F-S HVPE-GaN

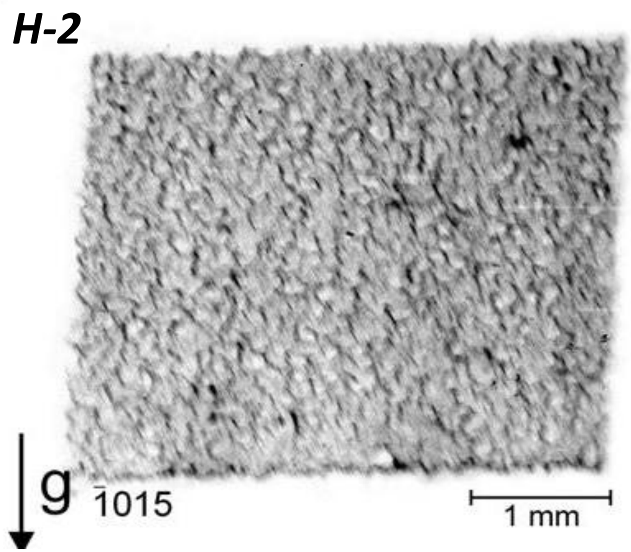


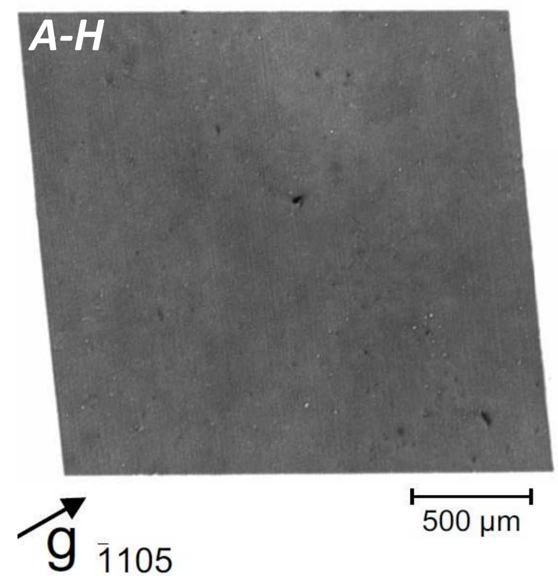


L. Kirste et al., ECS Transactions, 66 (1) 93-106 (2015)

Structural quality of F-S HVPE-GaN
Synchrotron white-beam X-ray topography (SWXRT)







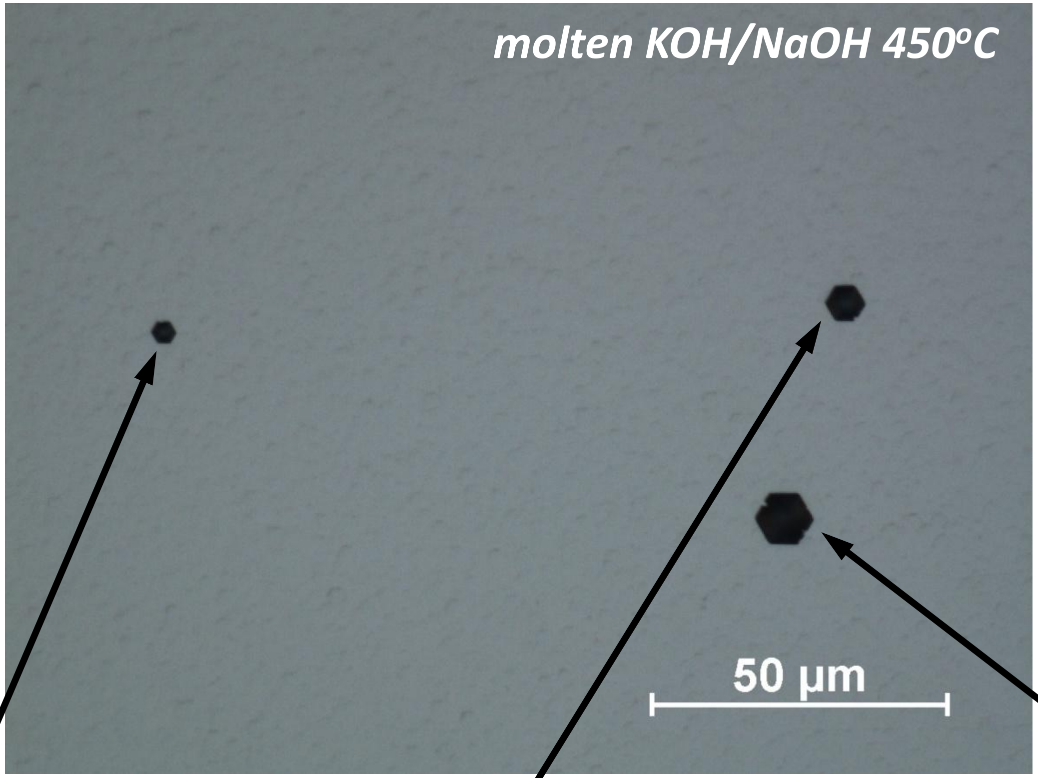
<u>cellular dislocation network</u>

The dislocation rearrangement into cell networks takes place under external or internal stress in the course of plastic relaxation.

Uniform gray contrast indicates a high degree of crystalline perfection

L. Kirste ECS Journal of Solid State Science and Technology, 4 (8) P324-P330 (2015)

Structural uniformity - etch pit distribution



EPD = $5x10^4$ cm^{-2}

J. Weyher,
T. Sochacki

Edge dislocation

Mixed dislocation

Screw dislocation

J. L. Weyher et al., Journal of Crystal Growth 305 (2007) 384–392

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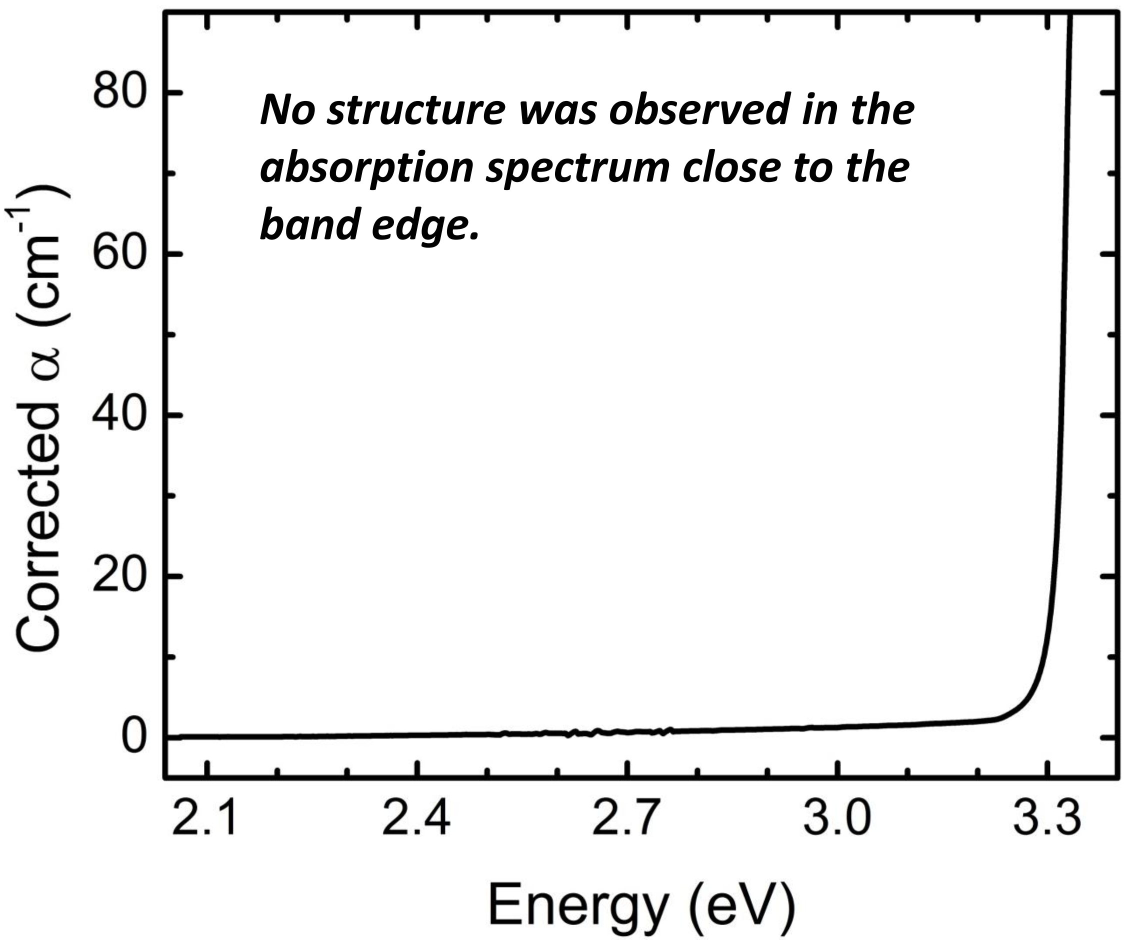
Room temperature transmission



-Hg(Xe) arc lamp source
-Princeton Instruments Acton SP2750 0.75 m high-resolution monochromator with 3600 grooves/mm grating

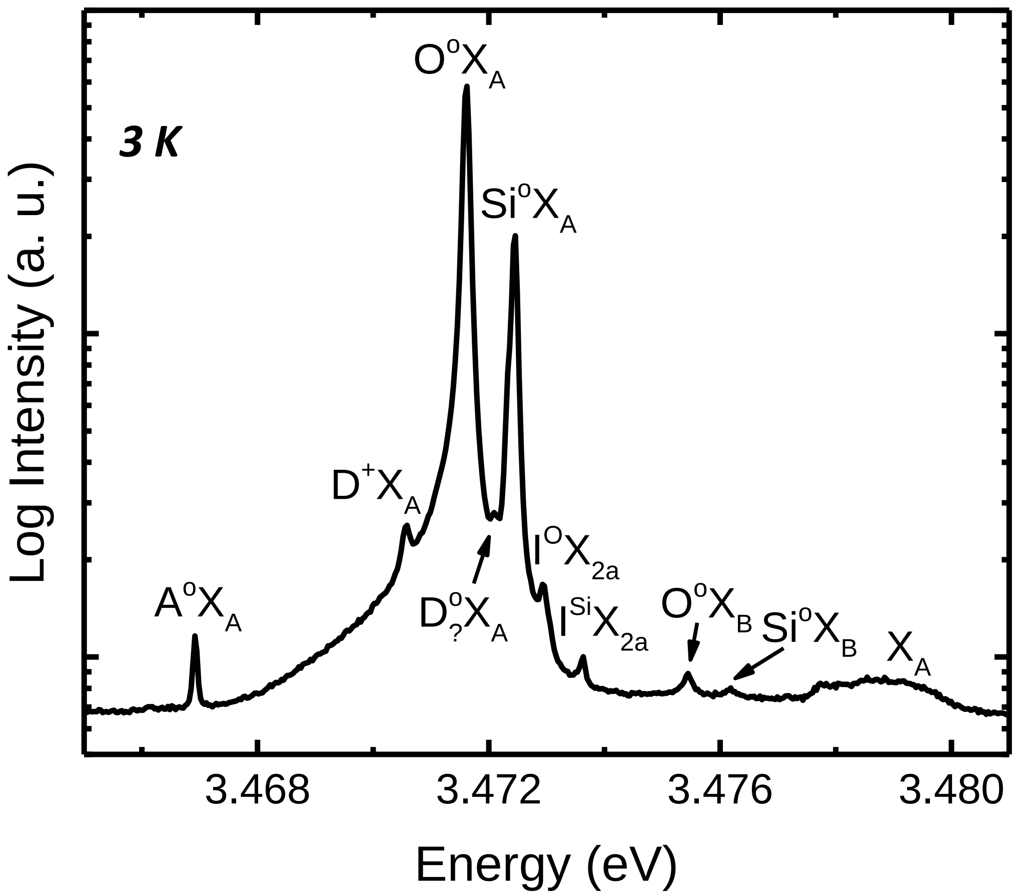
The absorption coefficient below the bandgap was measured to be less than 1 cm^{-1}

NC STATE UNIVERSITY
Department of Materials Science and Engineering

M. Bobea, Z. Bryan, I. Bryan R. Collazo, Z. Sitar

T. Sochacki et al., Appl. Phys. Expri 6, 075504 (2013)

Low temperature photoluminescence



two sharp donor bound exciton emission lines

acceptor bound exciton emission

free exciton emissions

NC STATE UNIVERSITY

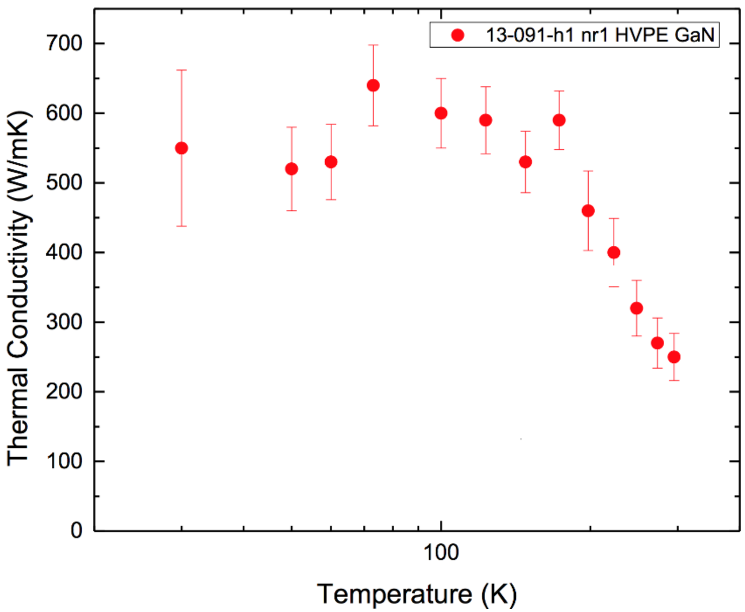
Department of Materials Science and Engineering

M. Bobea, Z. Bryan, I. Bryan R. Collazo, Z. Sitar

T. Sochacki et. al, Journal of Crystal Growth 394 (2014) 55–60

Thermal conductivity
by 3ω and hyper flash methods

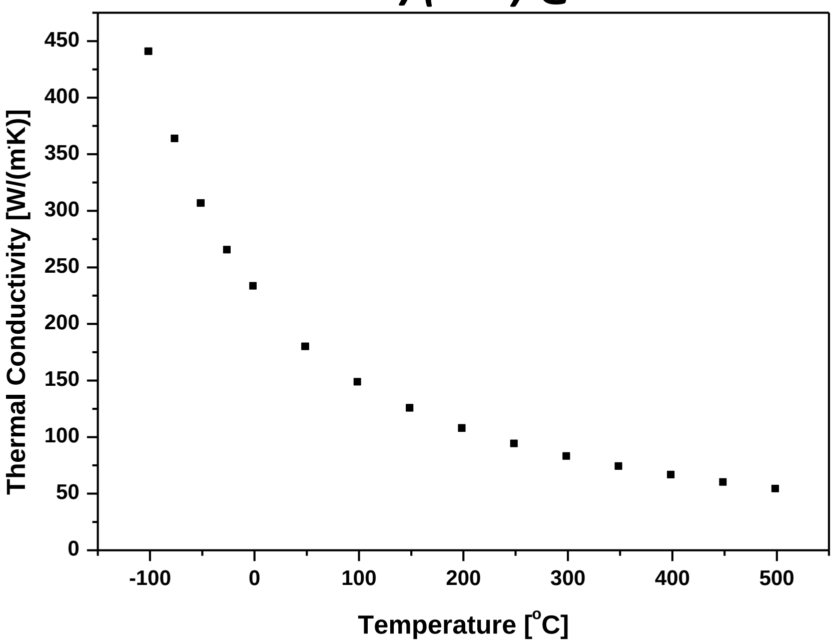
k = 250 ± 50 W/(m·K) @ room T



NC STATE UNIVERSITY
Department of Materials Science and Engineering

Z. Sitar

k > 200 W/(m·K) @ room T



PLANSEE

M. Seiss

T. Sochacki et al., Appl. Phys. Expri 6, 075504 (2013)

Thermal conductivity

Available online at www.sciencedirect.com

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Journal of Crystal Growth 284 (2005) 197–202

JOURNAL OF CRYSTAL GROWTH

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Investigation of thermal conductivity of GaN by molecular dynamics

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Available online 15 August 2005

Communicated by K. Nakajima

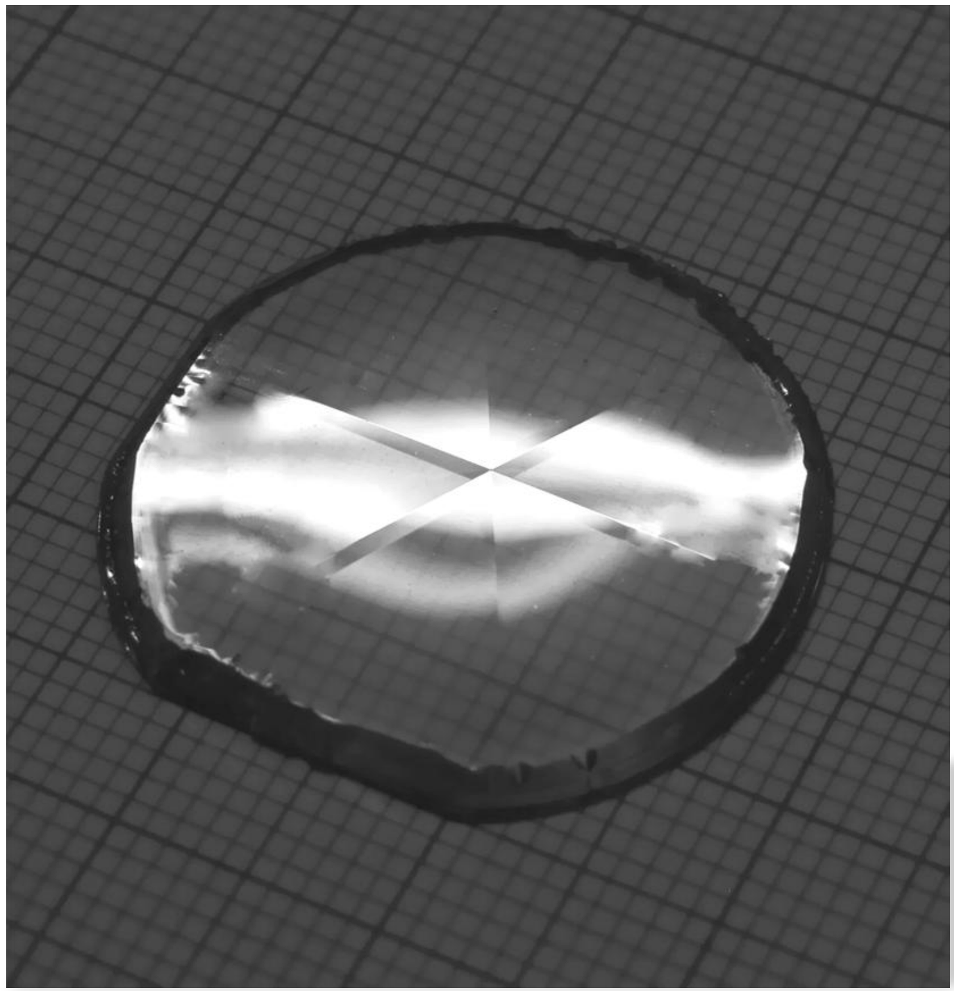
Abstract

Thermal conductivity of GaN was investigated by molecular dynamics simulation. We used Stillinger–Weber potentials, and Green-Kubo's formula was employed to calculate thermal conductivity. The results showed that the thermal conductivity of GaN at 300 K was in the range of $310 < \lambda < 380$ W/mK, which is higher than the reported experimental values. We also investigated the temperature dependence of thermal conductivity in the temperature range of 300–1200 K.

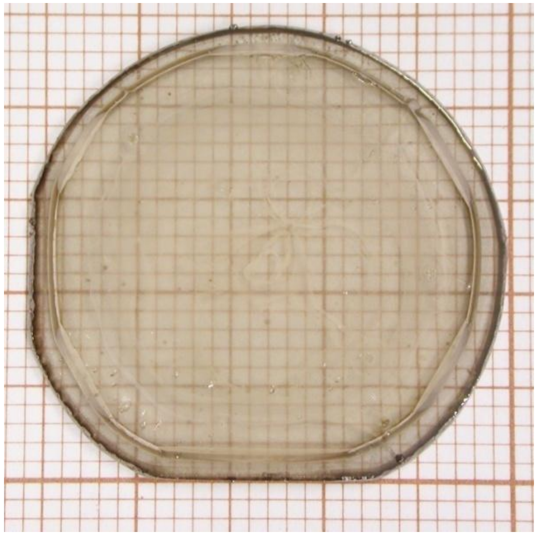
PACS: 78.66.Fd; 67.80.Gb

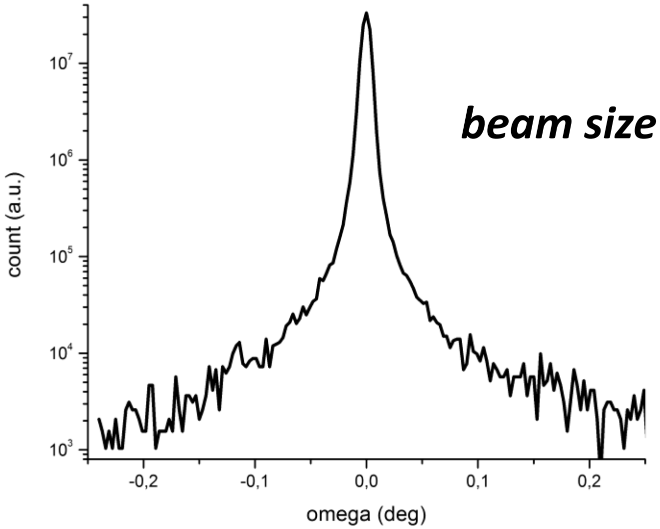
Keywords: A1. Molecular dynamics; A1. Thermal conductivity; B1. Gallium nitride

Doping in HVPE growth method



Doping: HVPE-GaN:Si





beam size 1x10 mm

Thickness: 600 µm
Growth rate: 120 µm/h

FWHM (002)
32.4 arcsec

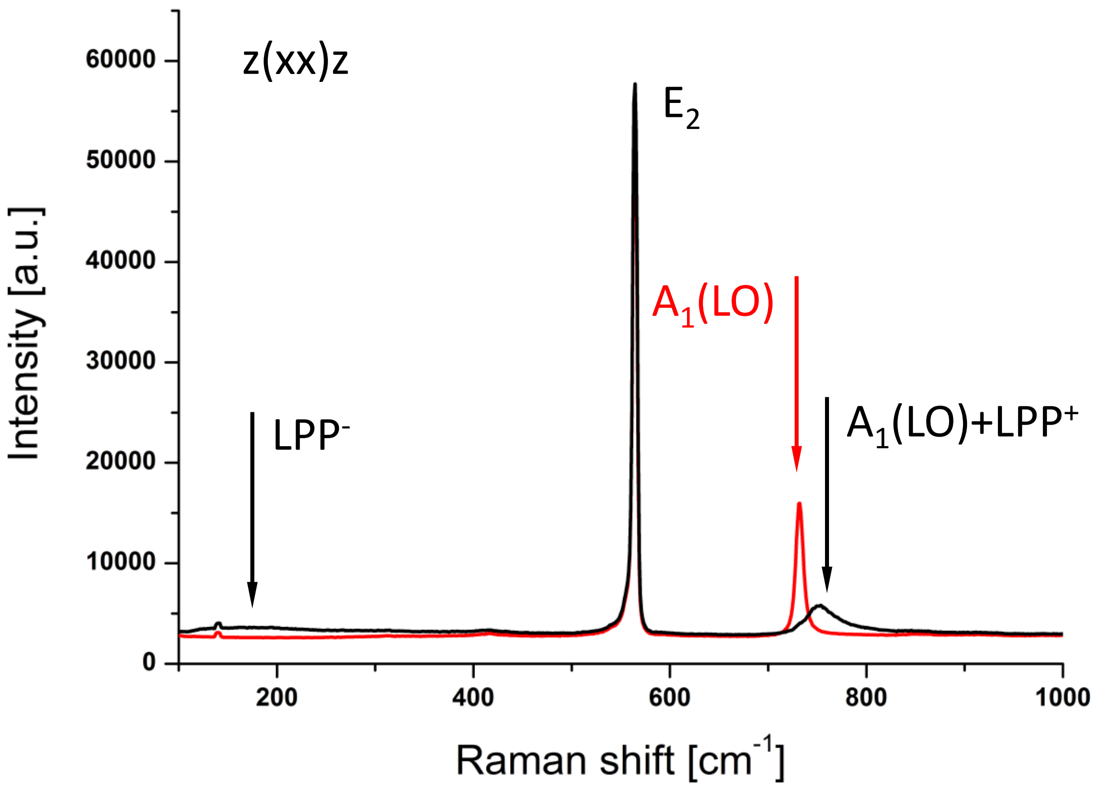
B. Łucznik, T. Sochacki, M. Amilusik, M. Fijałkowski, M. Iwińska, P. Kempisty, I. Grzegory

Free carrier concentration
Raman spectroscopy

Typical Raman spectrum for GaN crystal with:

$n < 2 \times 10^{17}$ cm^{-3}

$n > 2 \times 10^{17}$ cm^{-3}



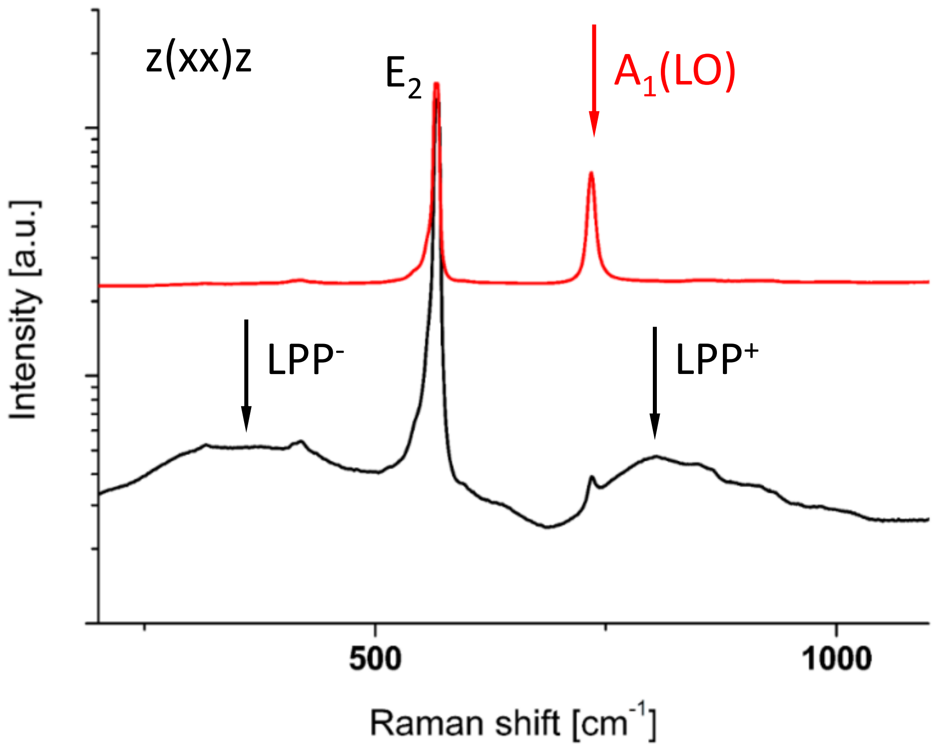
In doped semiconductors polar longitudinal modes are coupled with plasmons resulting in new LPP modes which positions are very sensitive to the free carrier concentration.

Raman spectroscopy versus Hall effect

Typical Raman spectrum for GaN crystal with:

$n < 2 \times 10^{17}$ cm^{-3}

$n > 2 \times 10^{17}$ cm^{-3}



Raman:

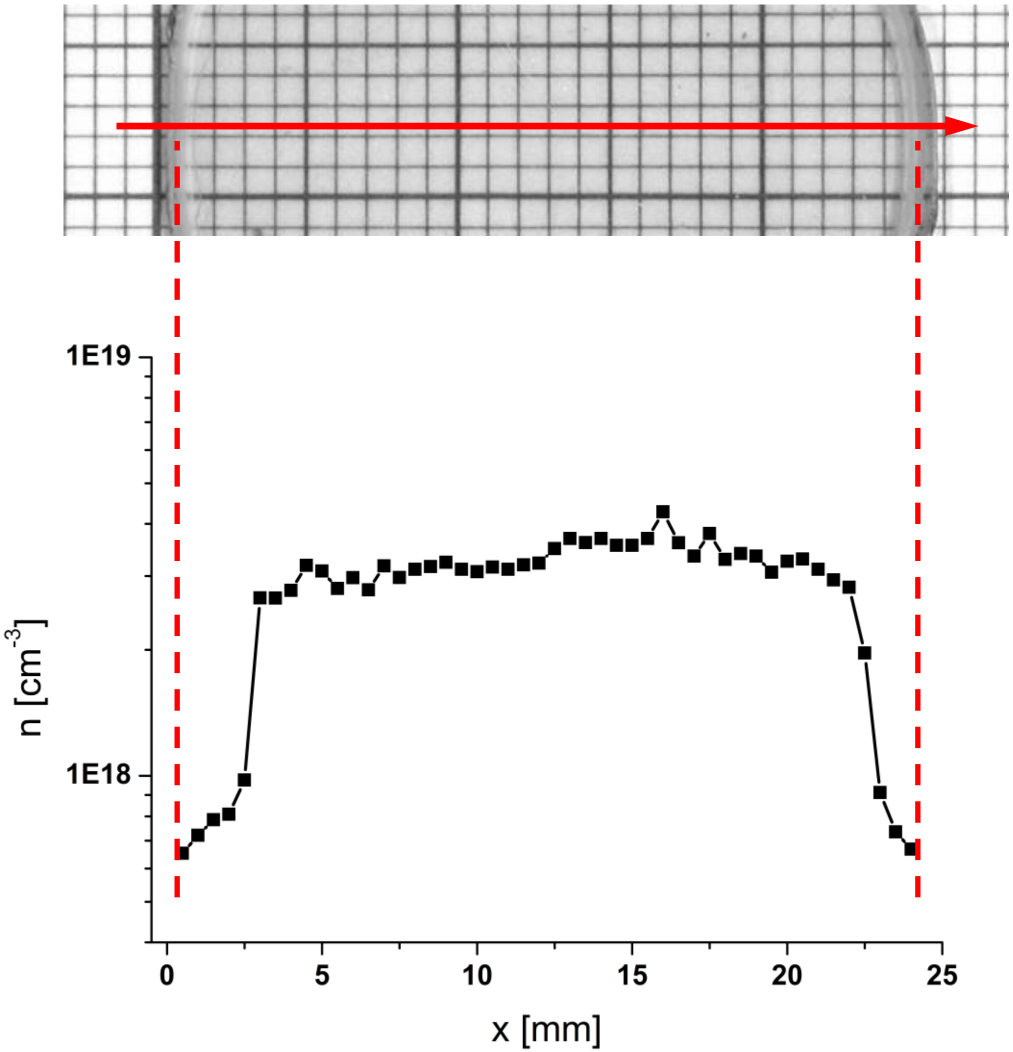
$n = 6 \times 10^{18}$ cm^{-3}

Hall:

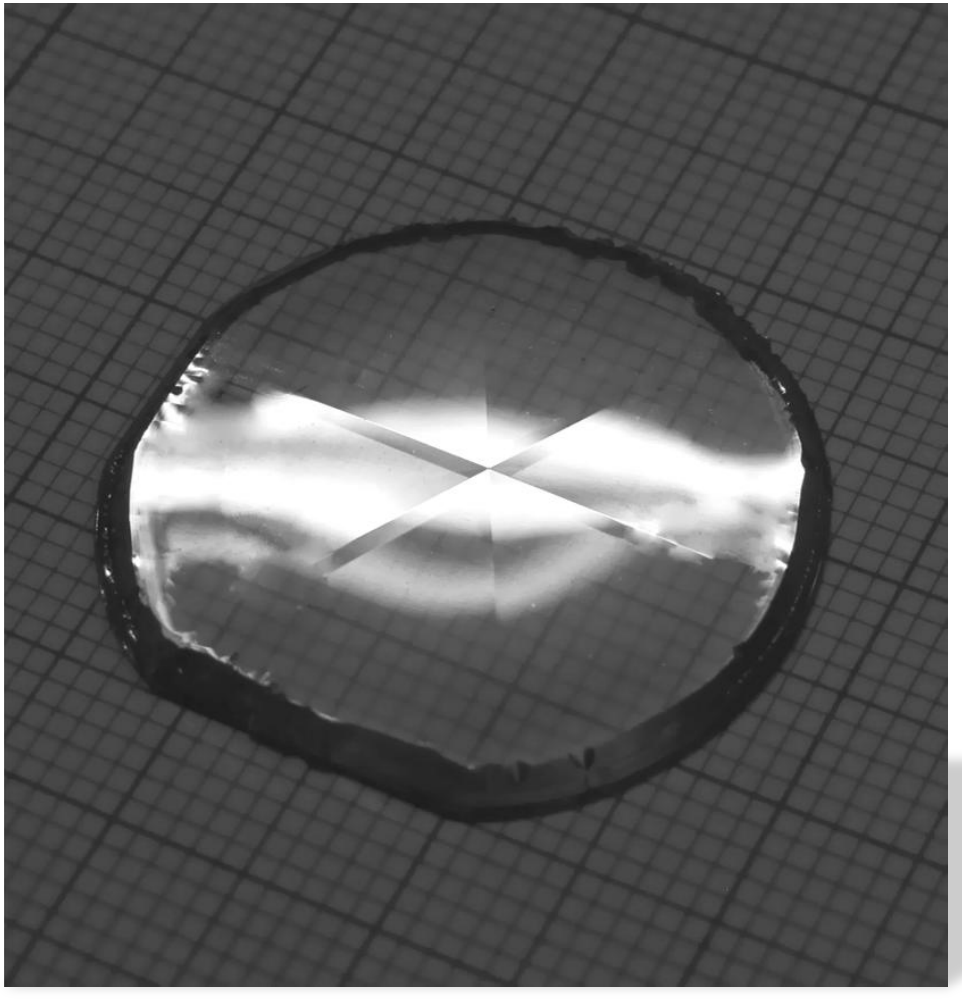
$n = 5.7 \times 10^{18}$ cm^{-3}

$\mu = 170$ [cm^2/Vs]

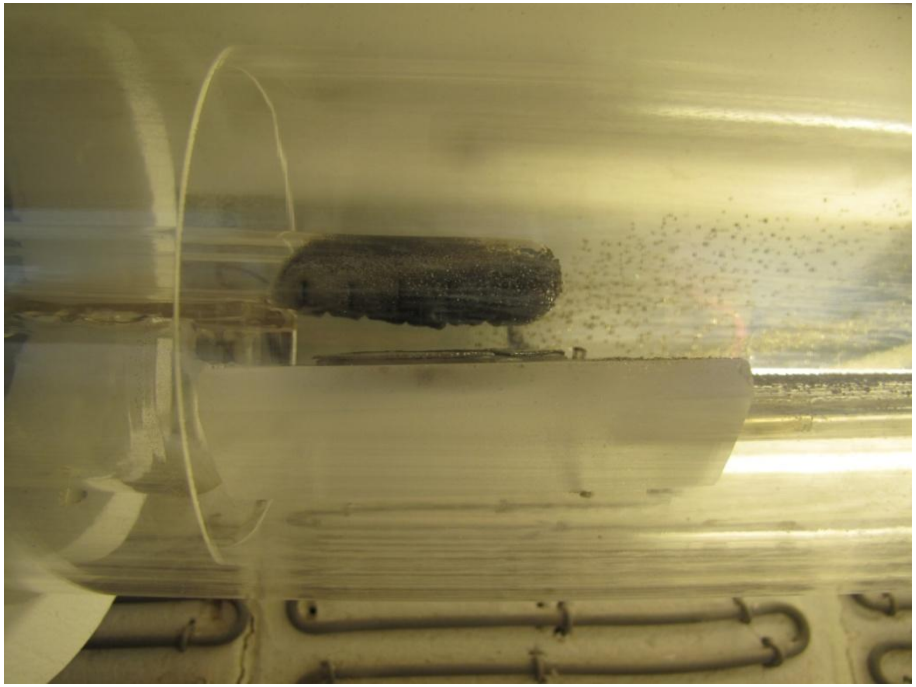
Free carrier concentration by Raman spectroscopy

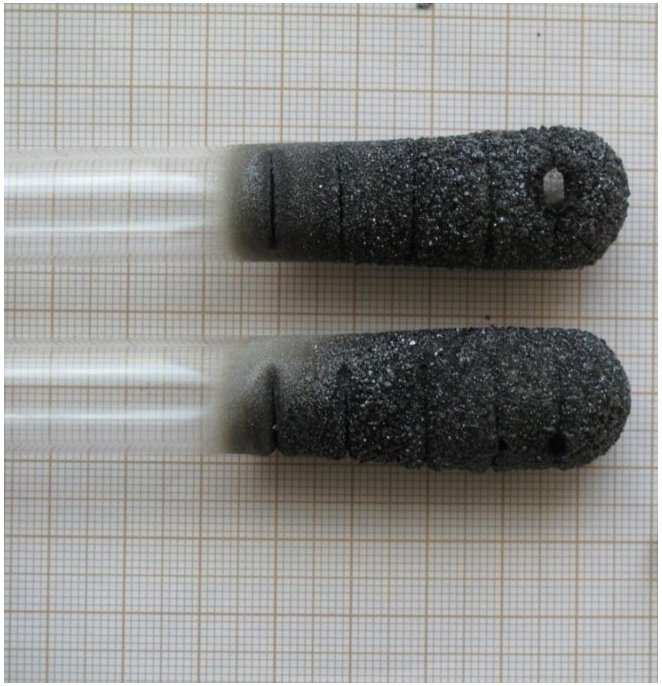


Limiting factors of HVPE method



Parasitic deposition

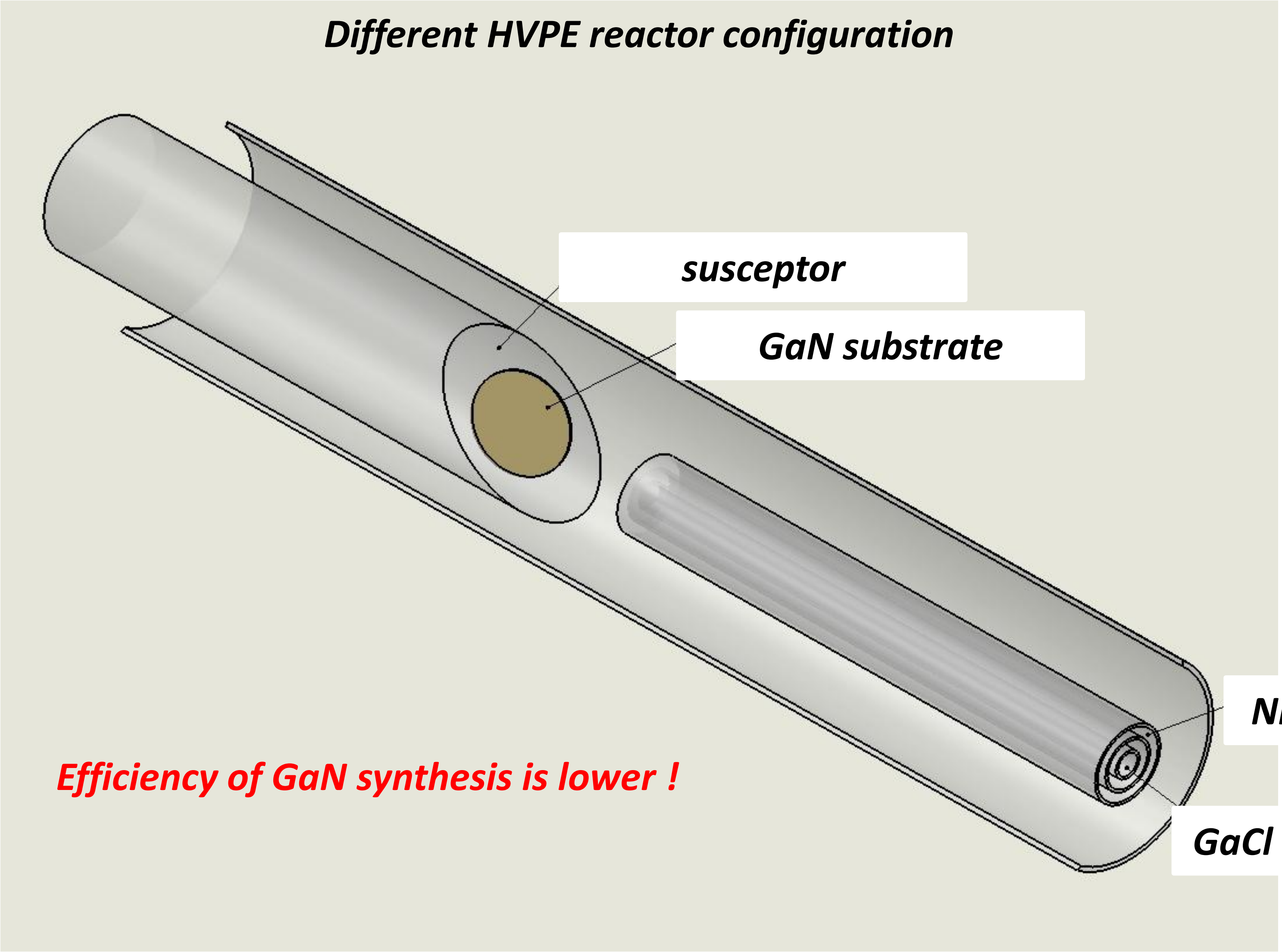




150-250 µm/h 10 - 6 h

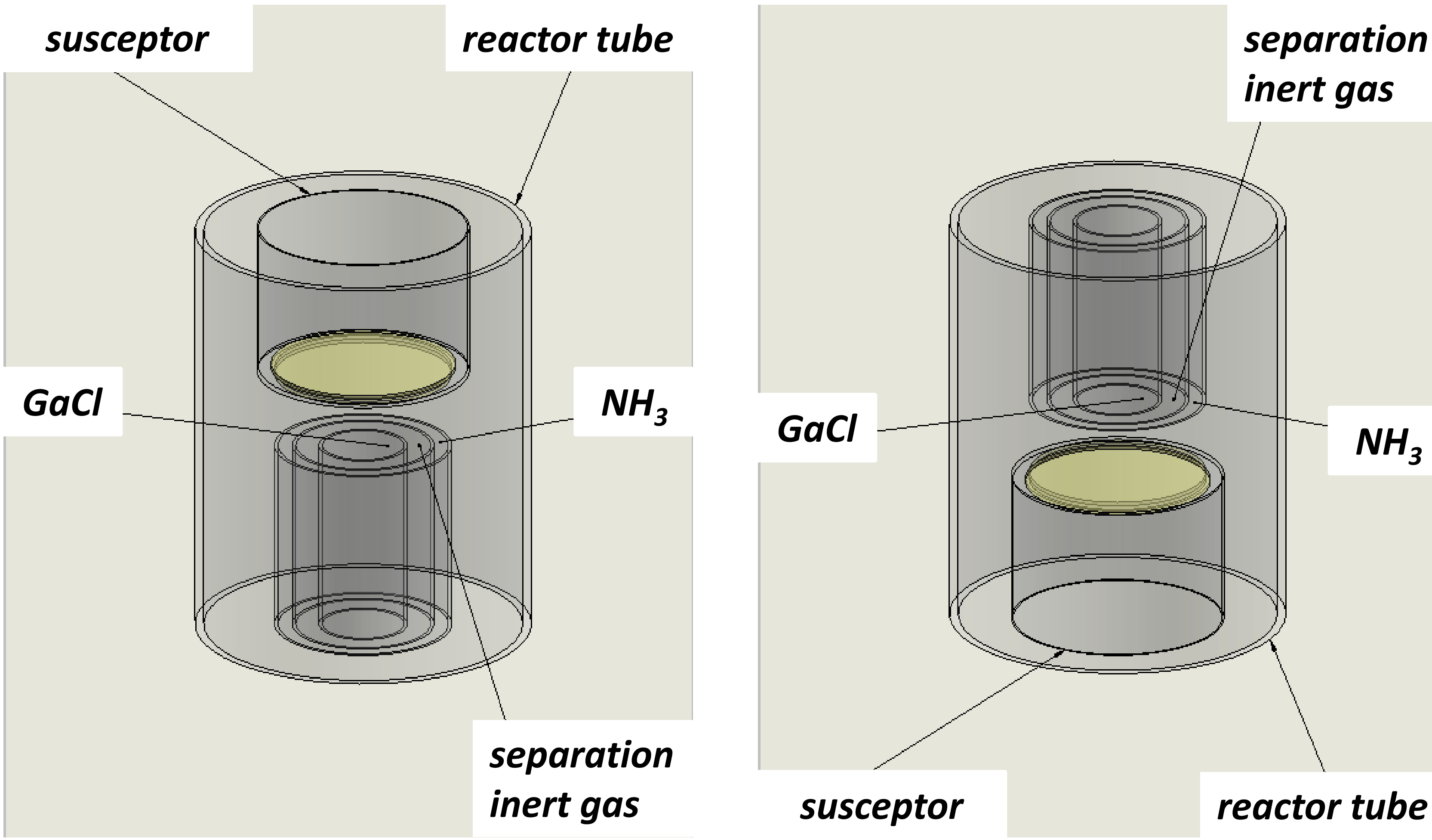
250-380 µm/h 6 - 2 h

Parasitic deposition

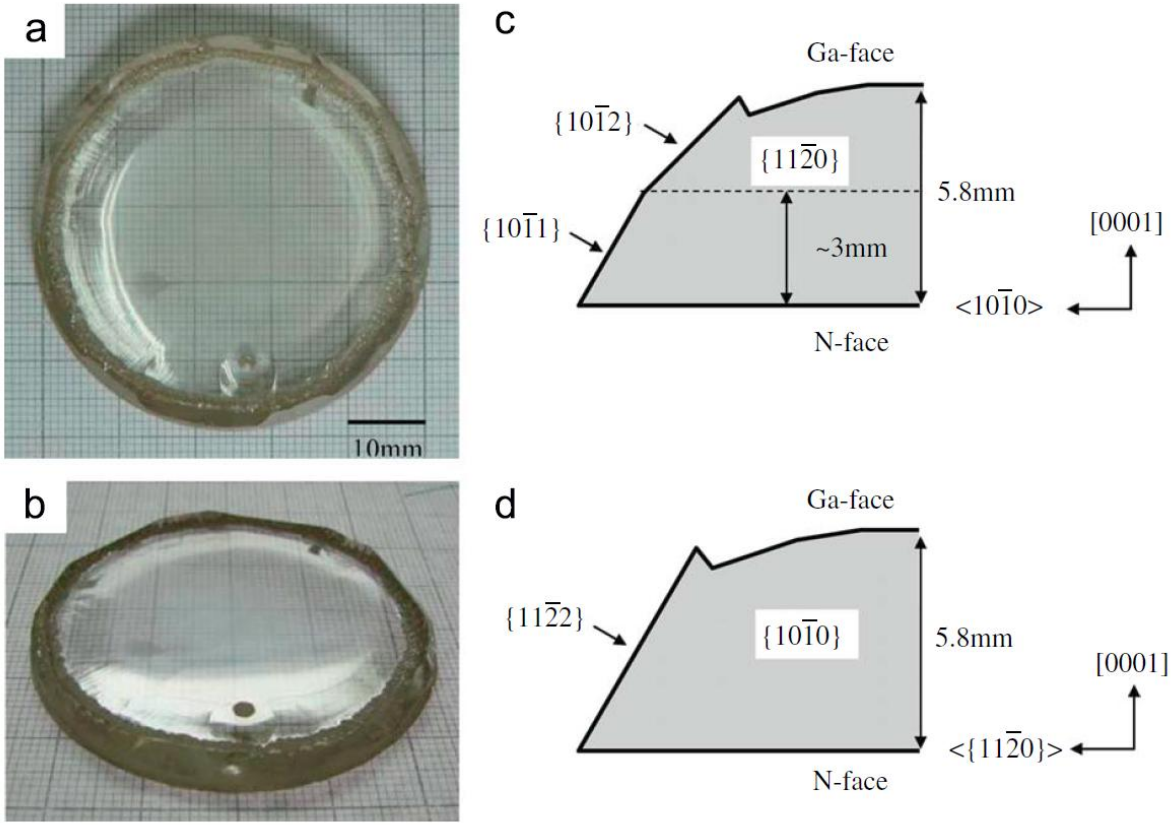


Parasitic deposition

Different HVPE reactor configuration



Parasitic deposition

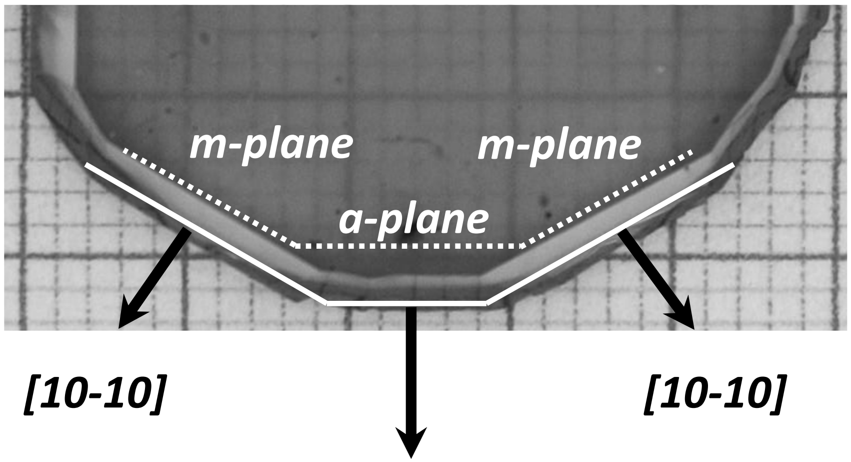


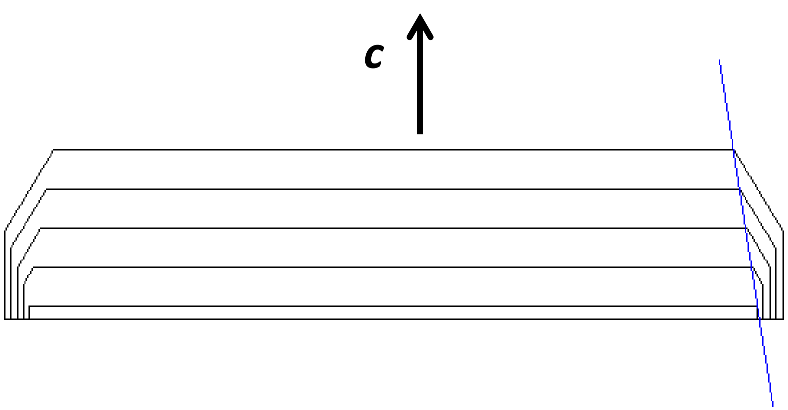
In general, a parasitic growth of polycrystalline GaN in a growth reactor is one of the major problems for bulk GaN crystals growth by HVPE.
An optimization of gas nozzles configurations and flow rates can solve this problem, so the parasitic nucleation was not a severe problem.

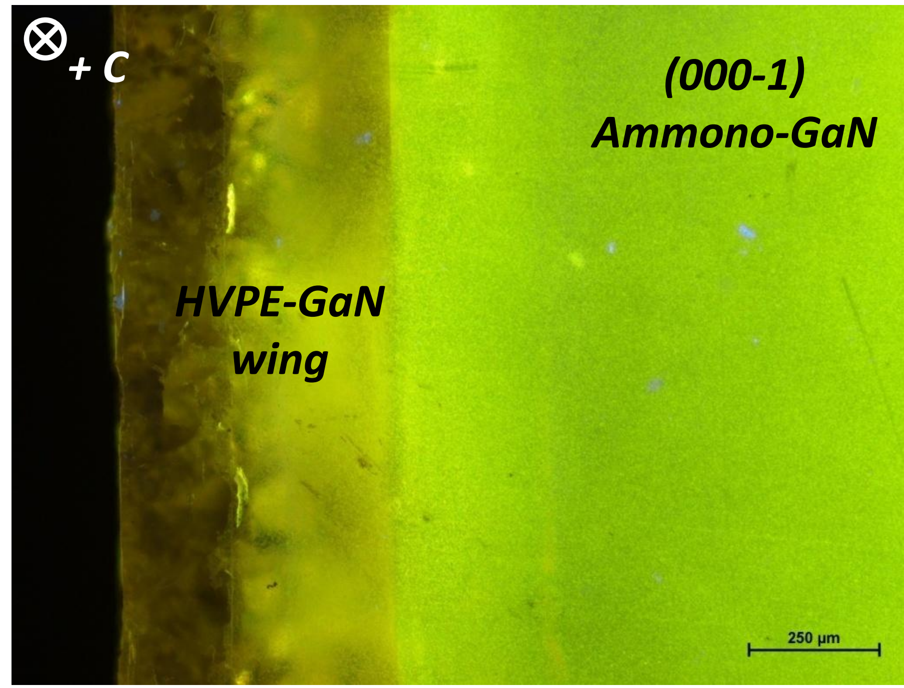
K. Fujito et al., Journal of Crystal Growth 311 (2009) 3011–3014

Anisotropy of the growth

dodecagon shape*



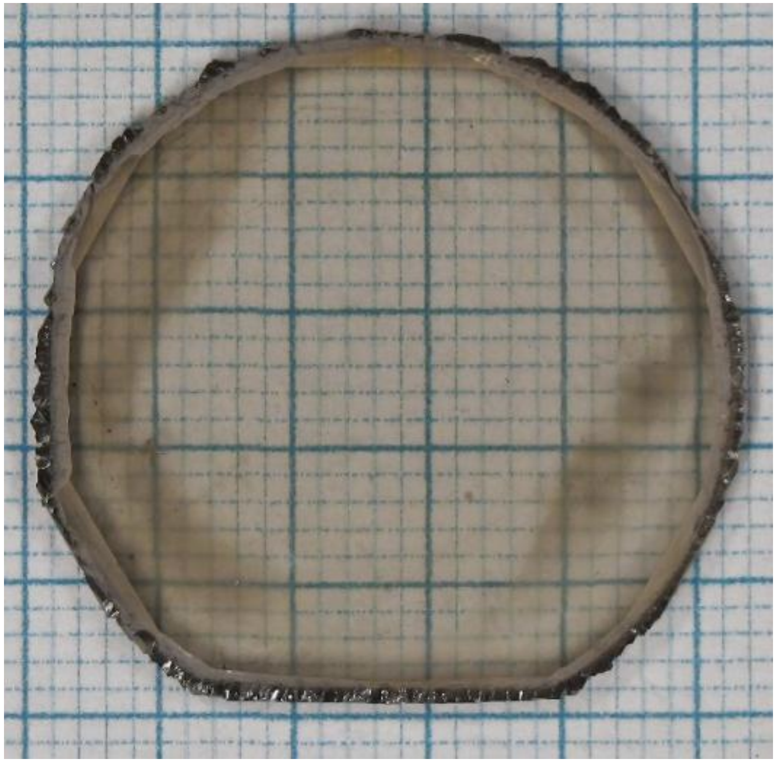


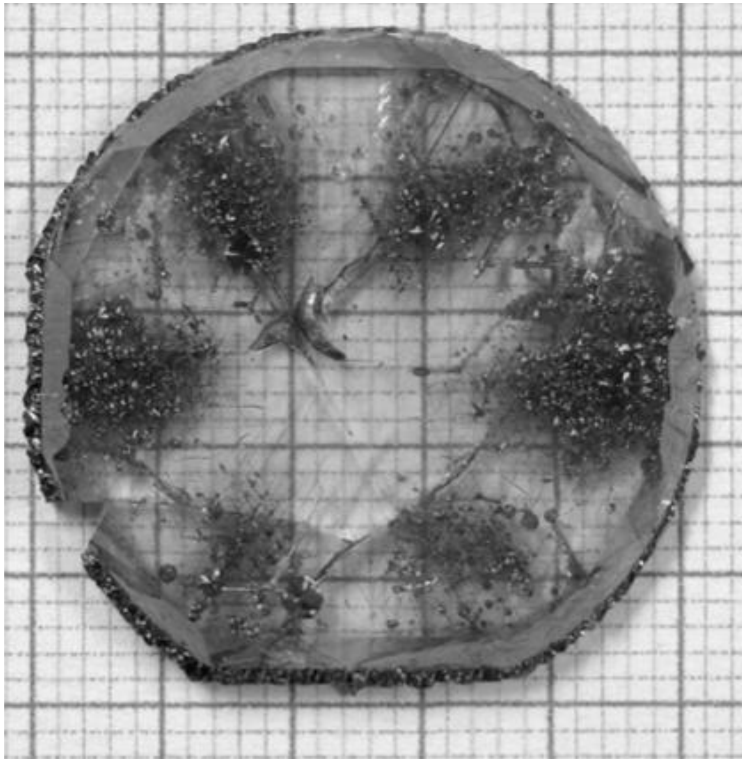


*** K. Fujito et al., Journal of Crystal Growth 311 (2009) 3011–3014**

Anisotropy of the growth

Same thicknesses of deposited layers – 1.5 mm

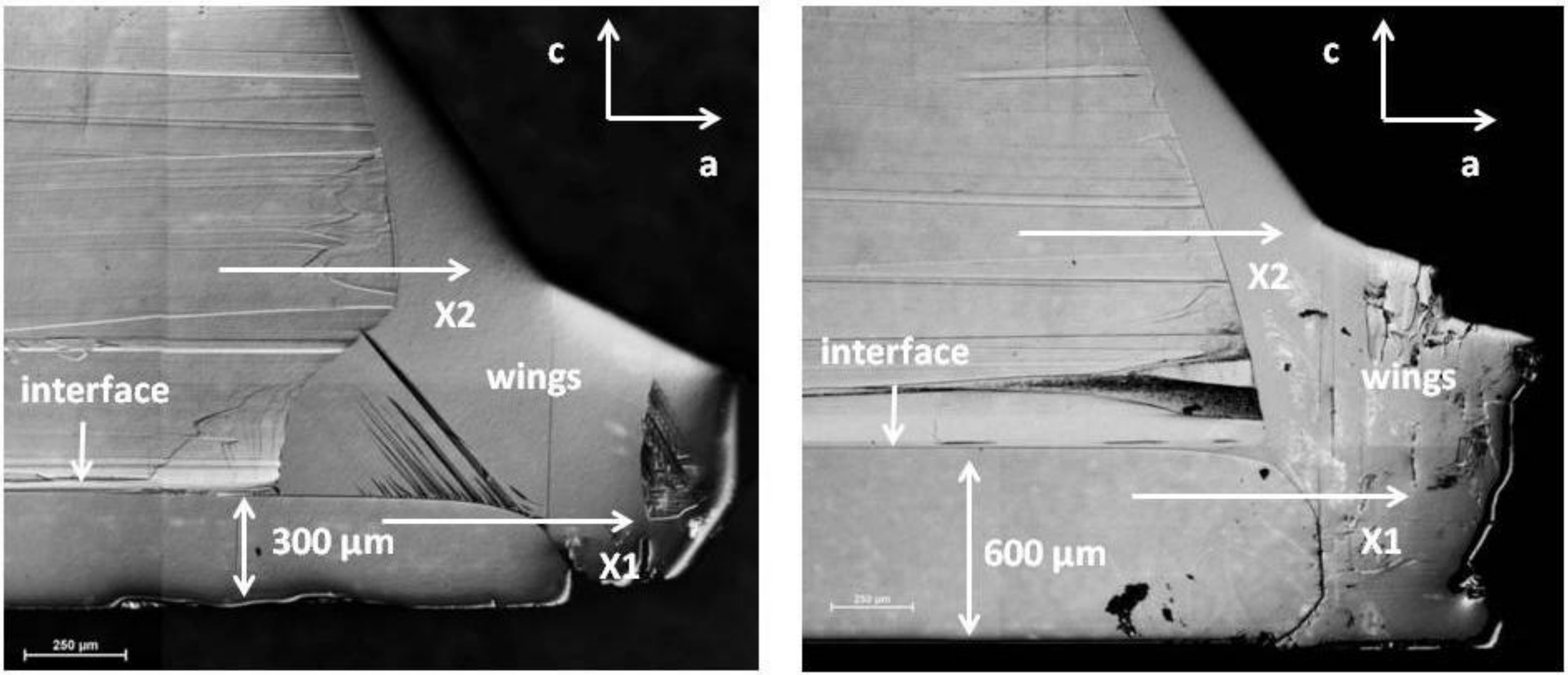




thinner seed – 300 µm ***thicker seed – 600 µm***

dodecagon shape

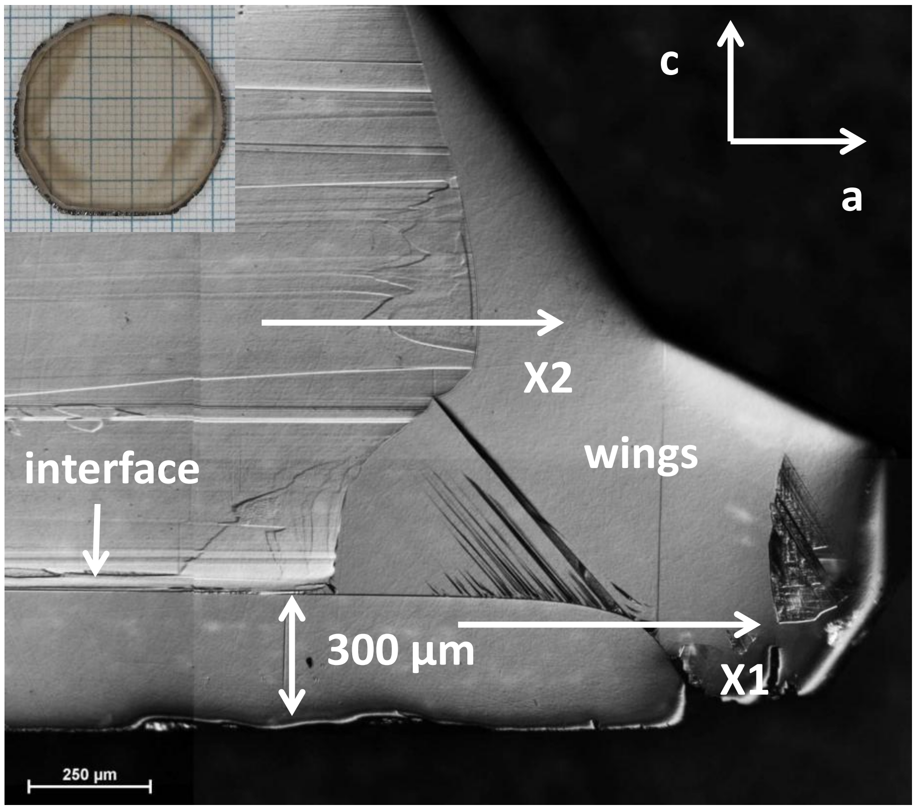
Anisotropy of the growth

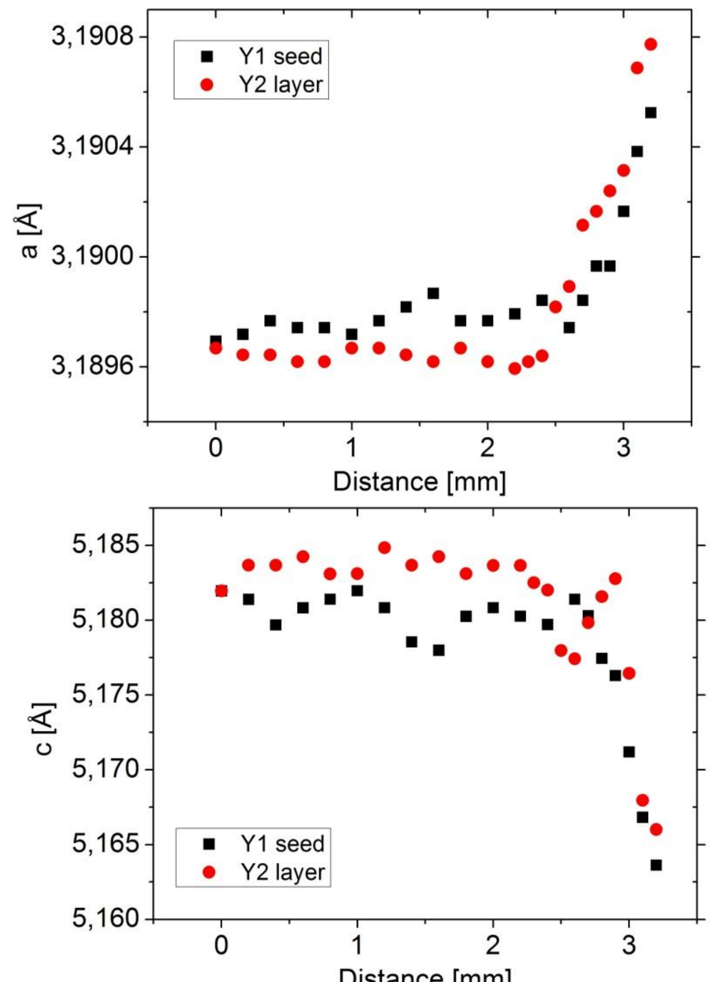


T. Sochacki et al., Phys. Status Solidi B 252, No. 5 (2015) 1172

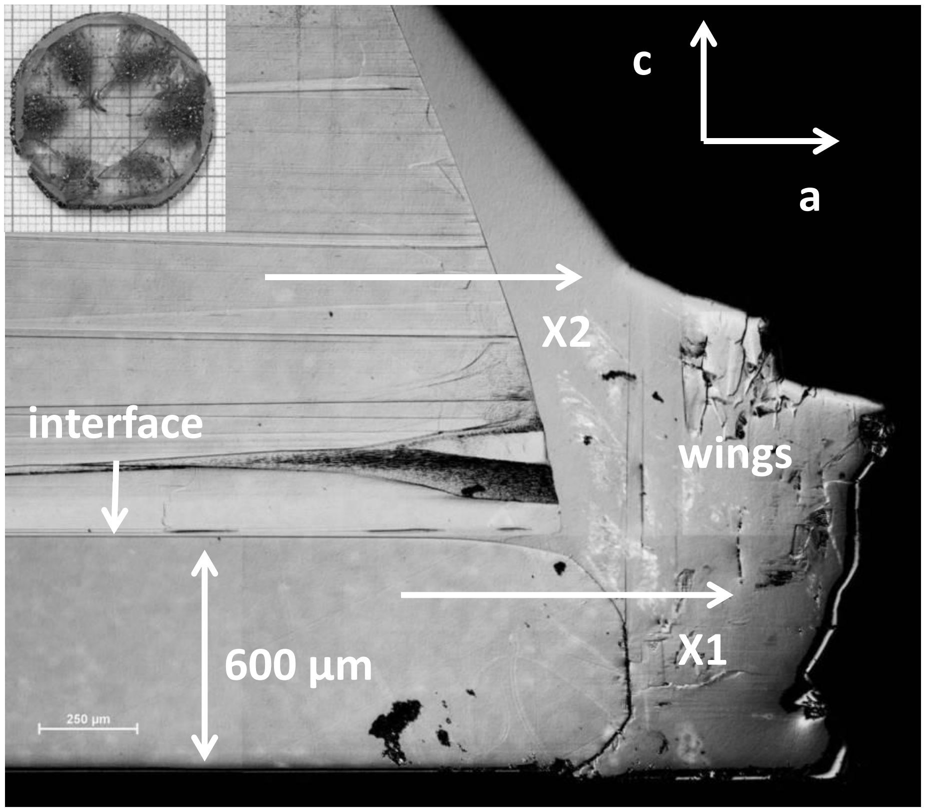
Anisotropy of the growth

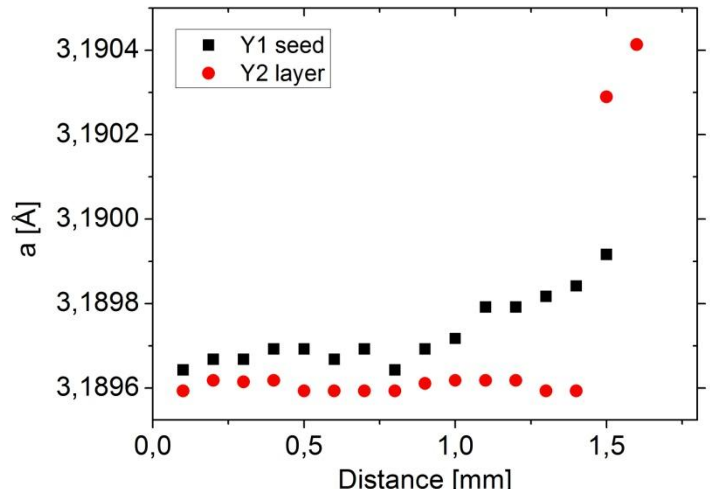
Increase of "a" lattice parameter is accompanied with decrease of "c" parameter.
It is typical for elastic strain of a system.

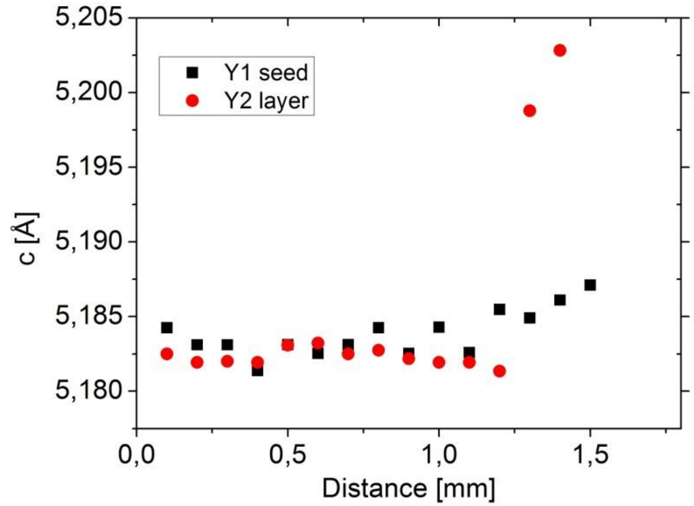




Anisotropy of the growth







J. Domagała, IP PAS

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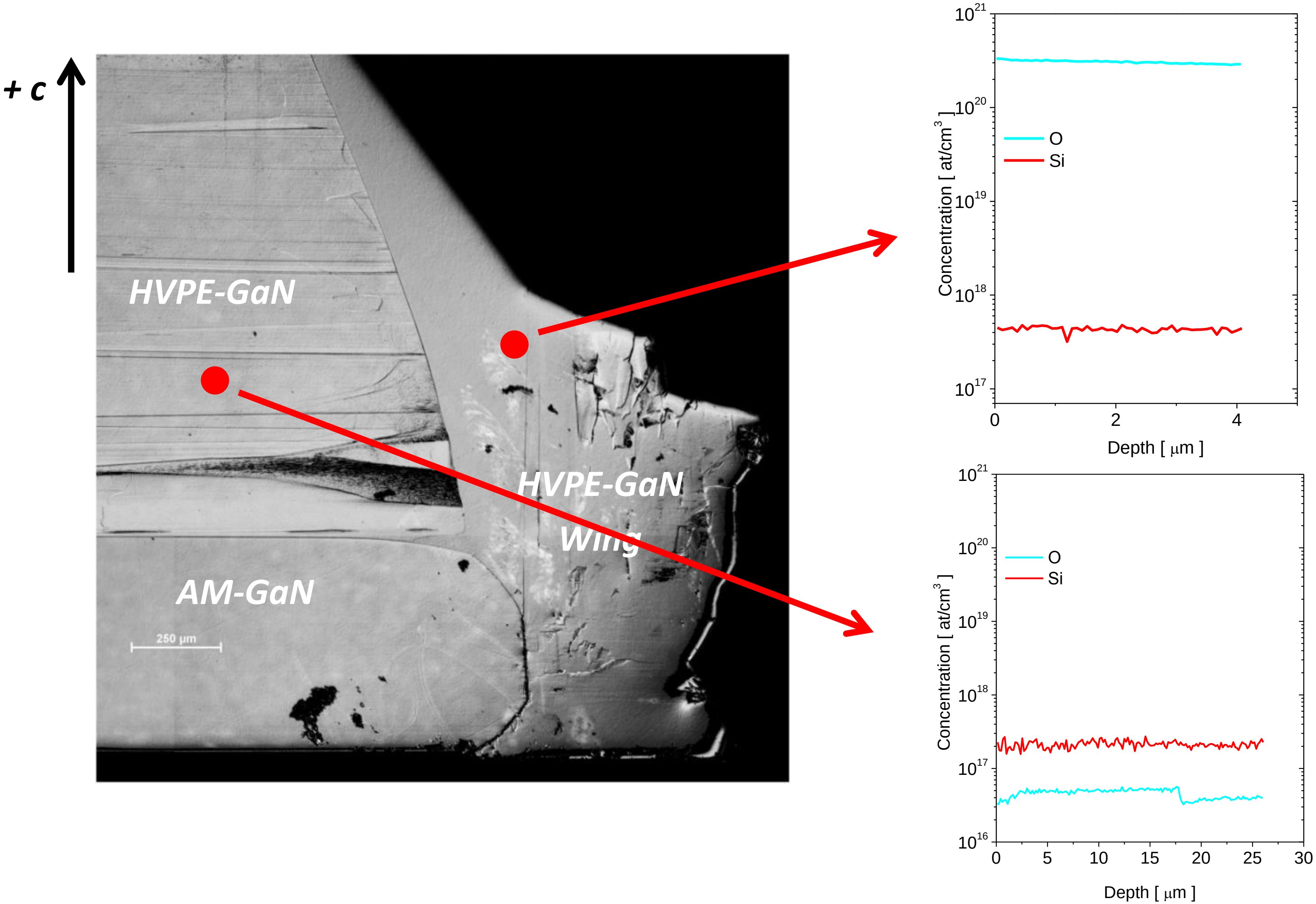
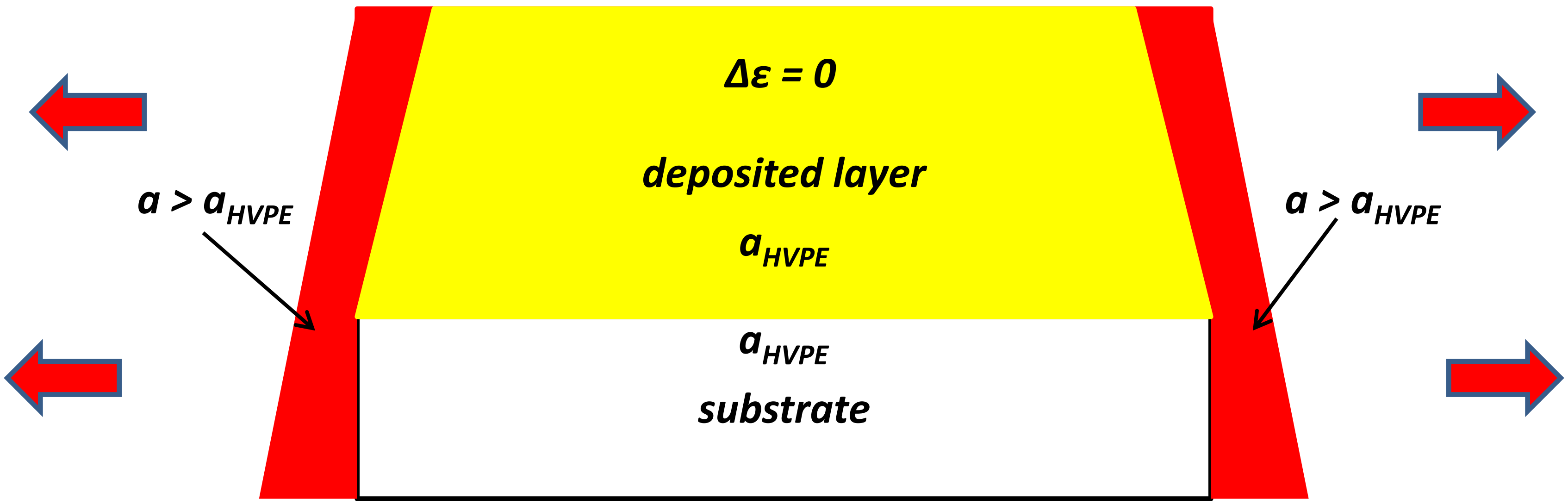
Anisotropy of the growth



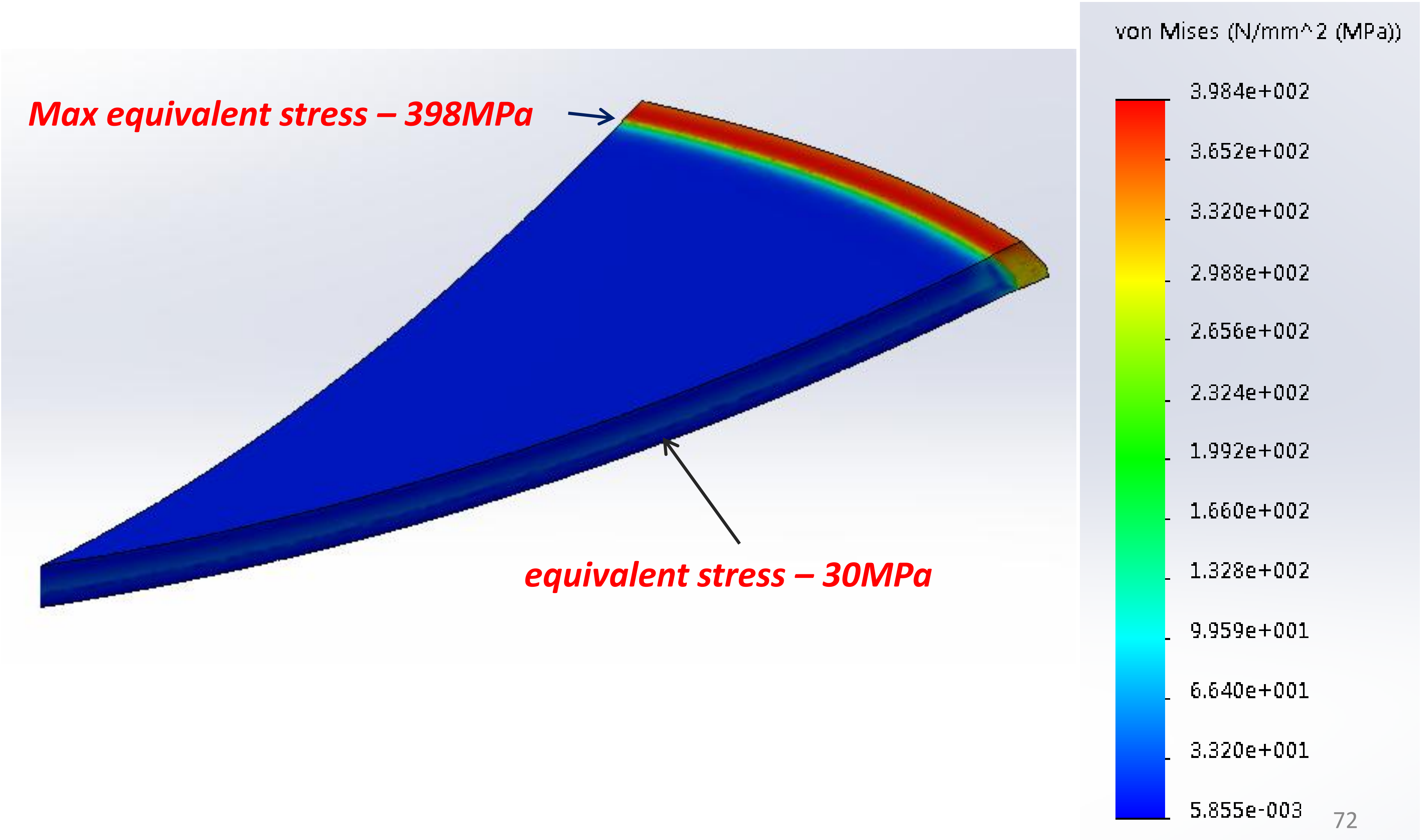
HVPE-GaN growth model



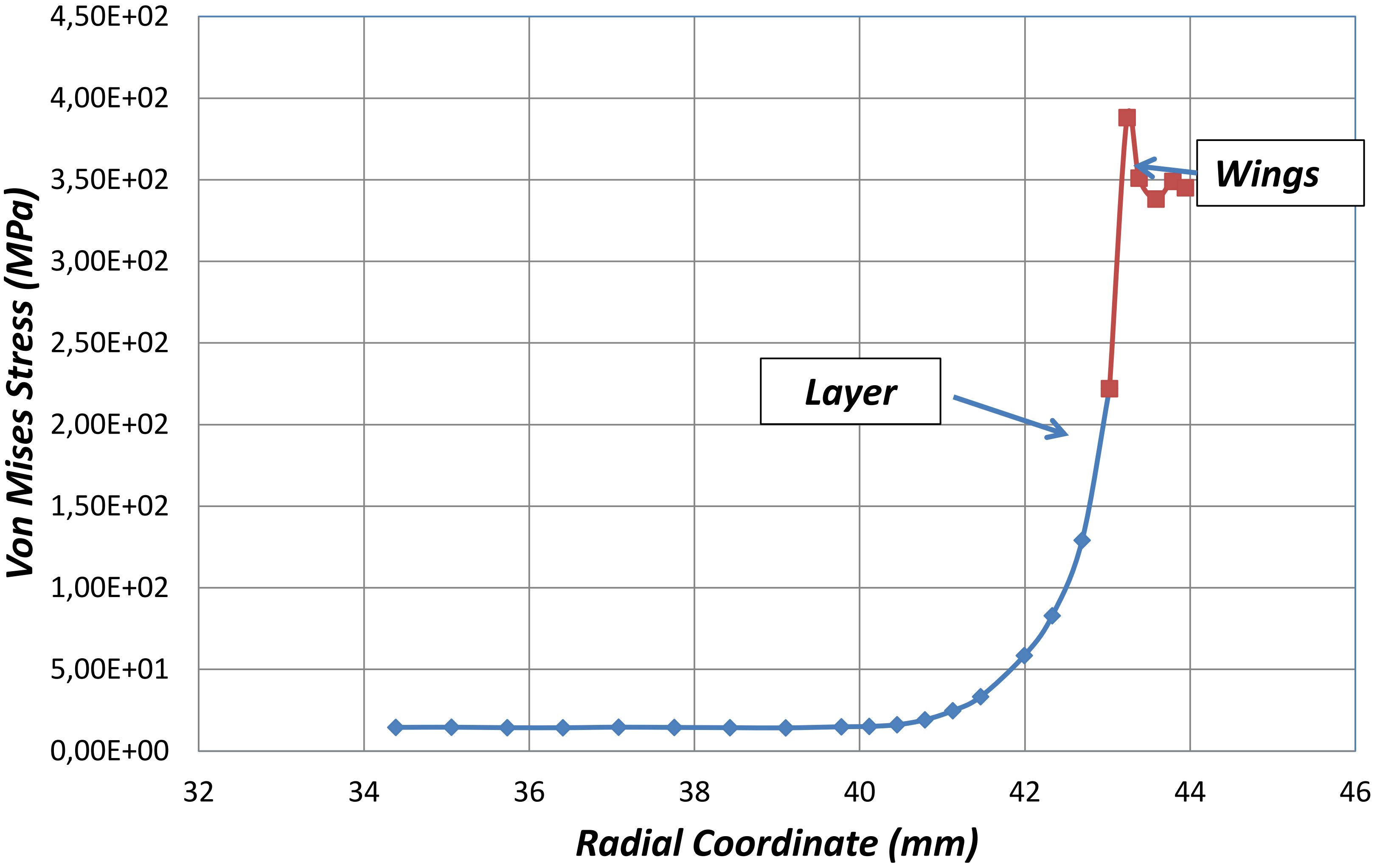
- the HVPE-GaN seed&layer are under tensile stress derived from wings;
plastic deformation can occur in the HVPE-GaN seed&layer.

Numerical simulation

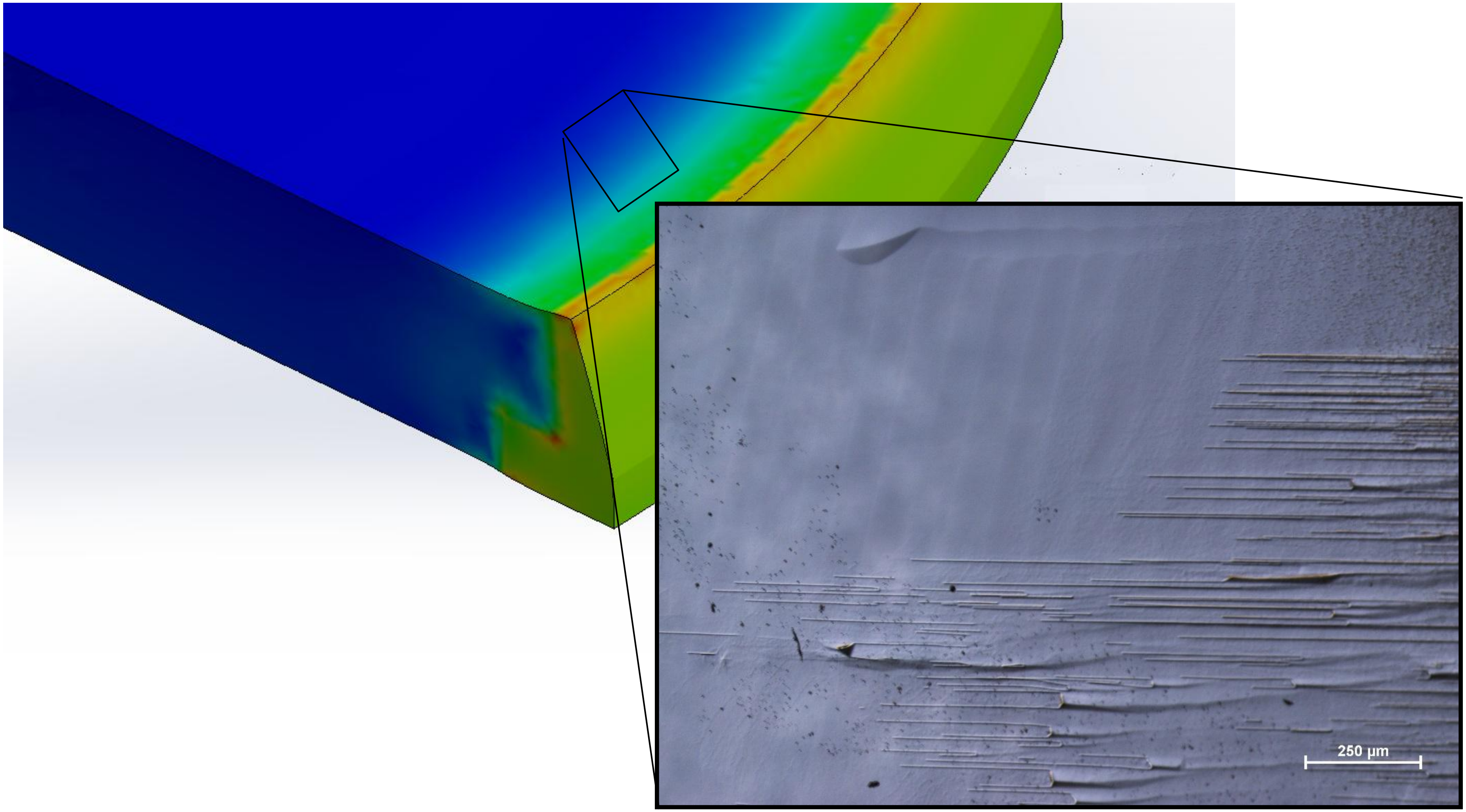
4-inch substrate



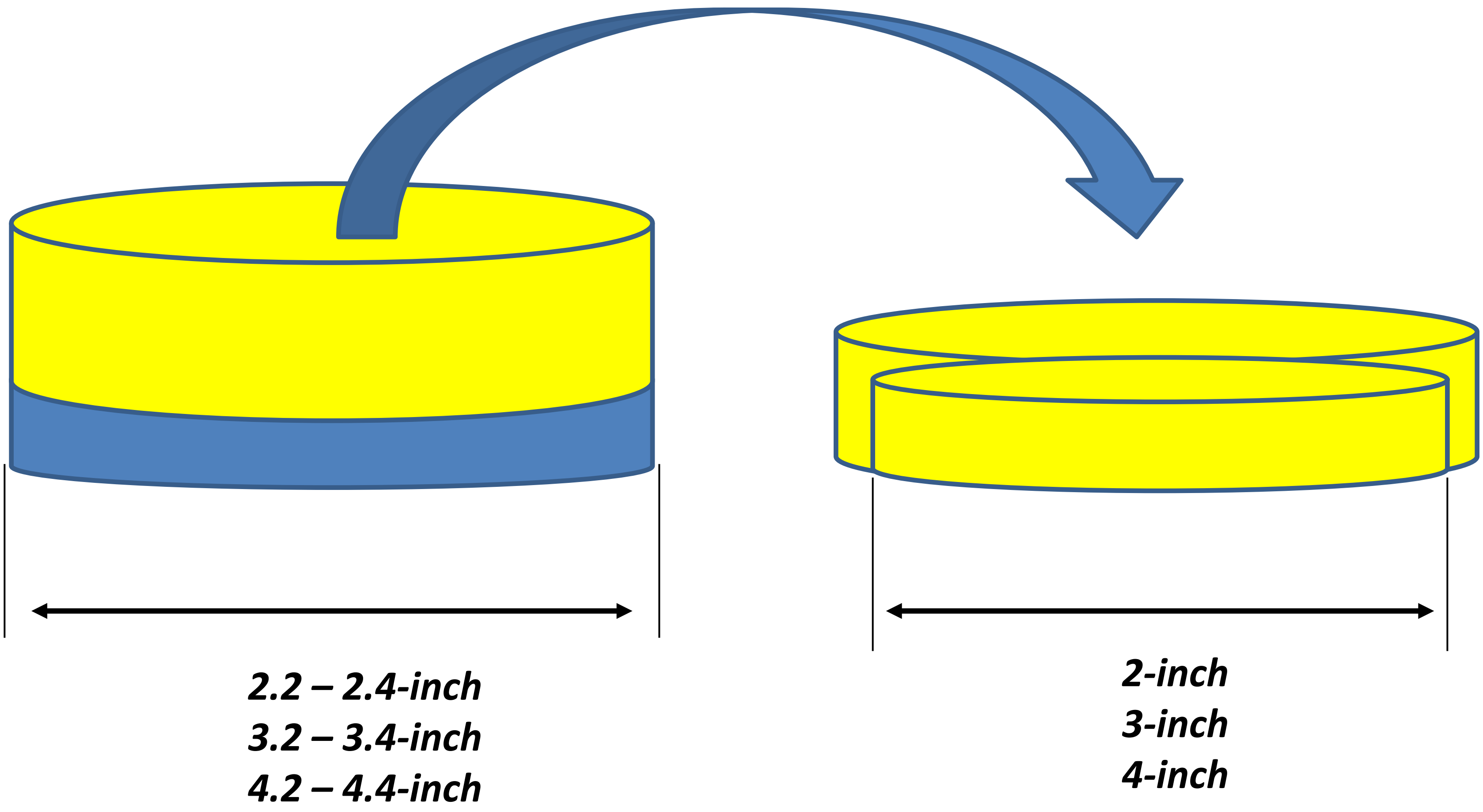
Stress Distribution



Negative role of wings



HVPE: wafer to wafer technology



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Potential solutions
Challenges

Concentration of impurities as well as the types of impurities are different on c-plane and on non-polar and semi-polar facets.

This causes stress in the growing crystal.

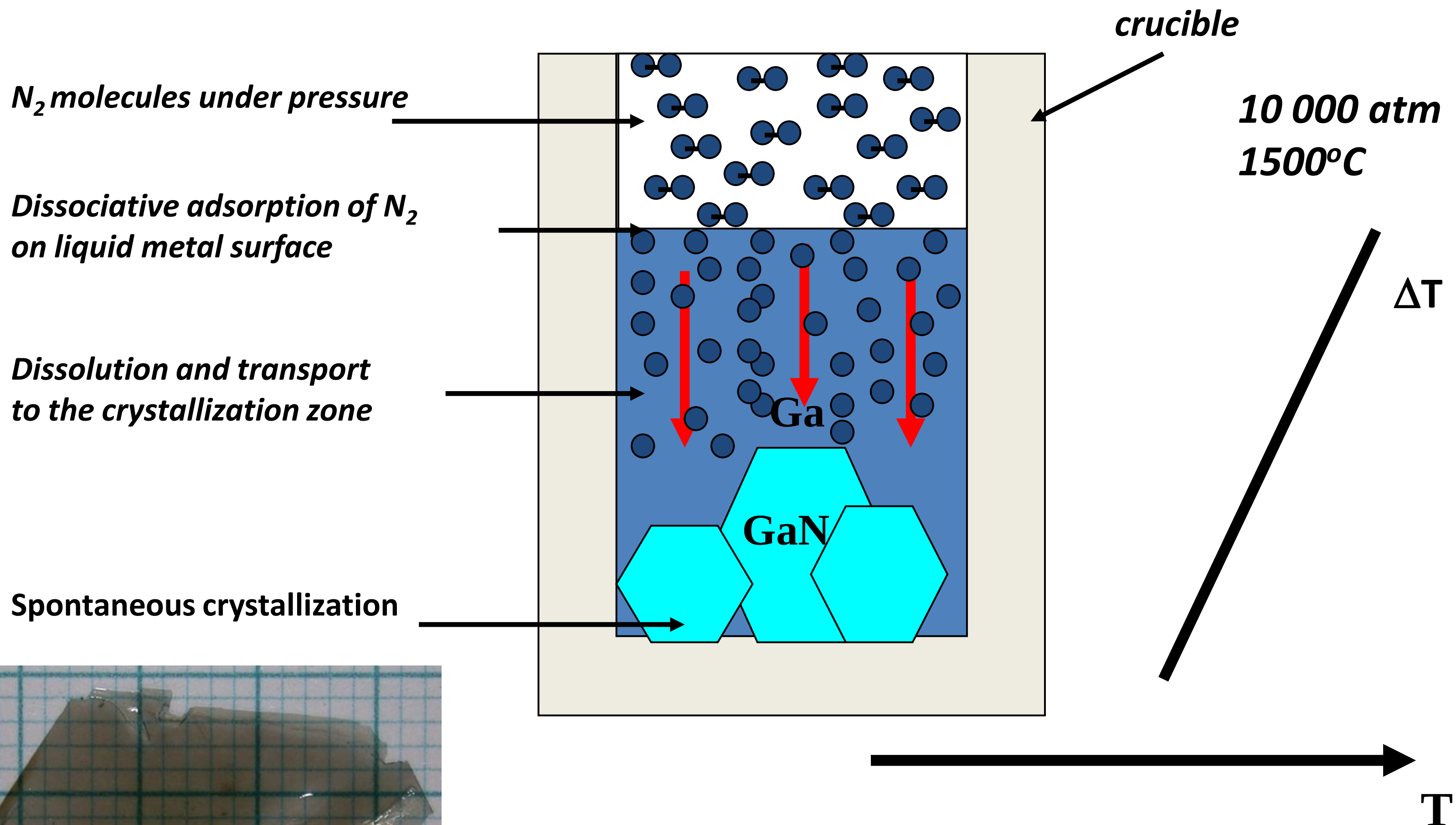
Uniform doping on all GaN facets can be helpful (Fermi level control).

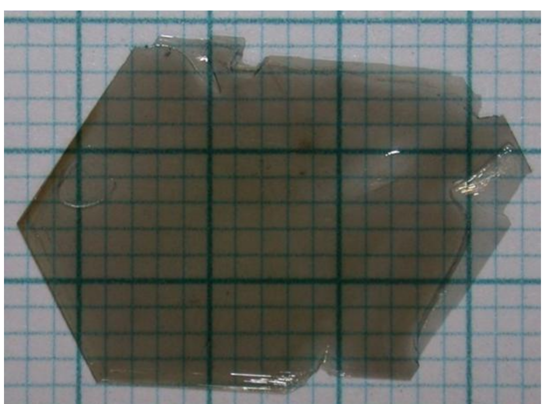
prof. Z. Sitar

Lattice constants engineering should be introduced.

prof. K. Kakimoto

High Nitrogen Pressure Solution (HNPS)

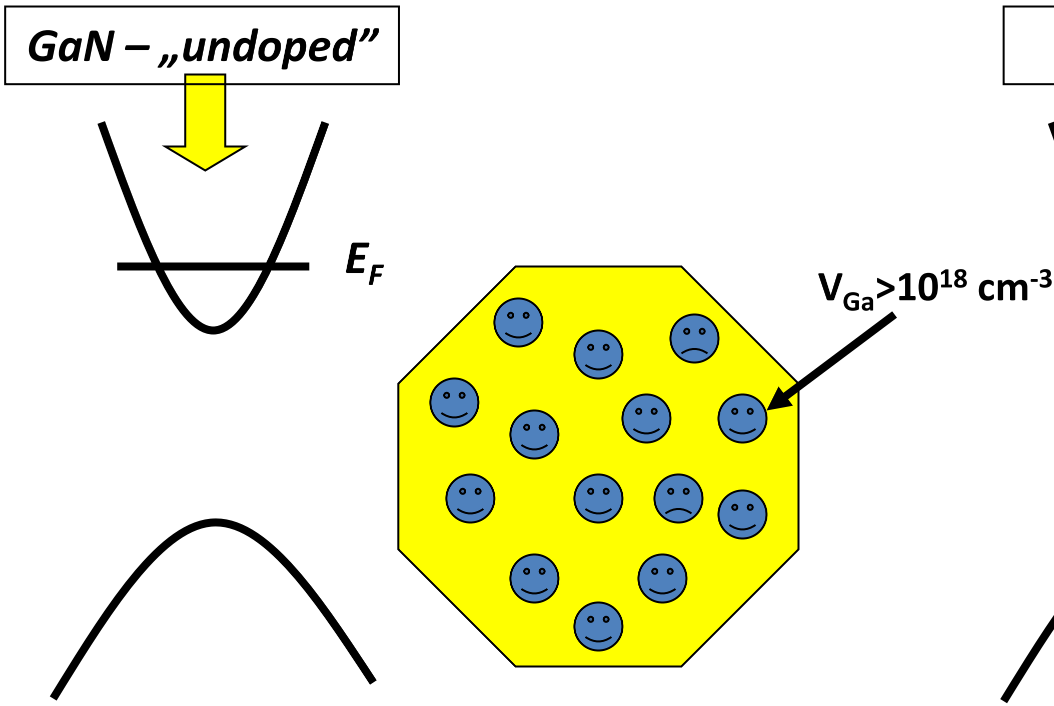


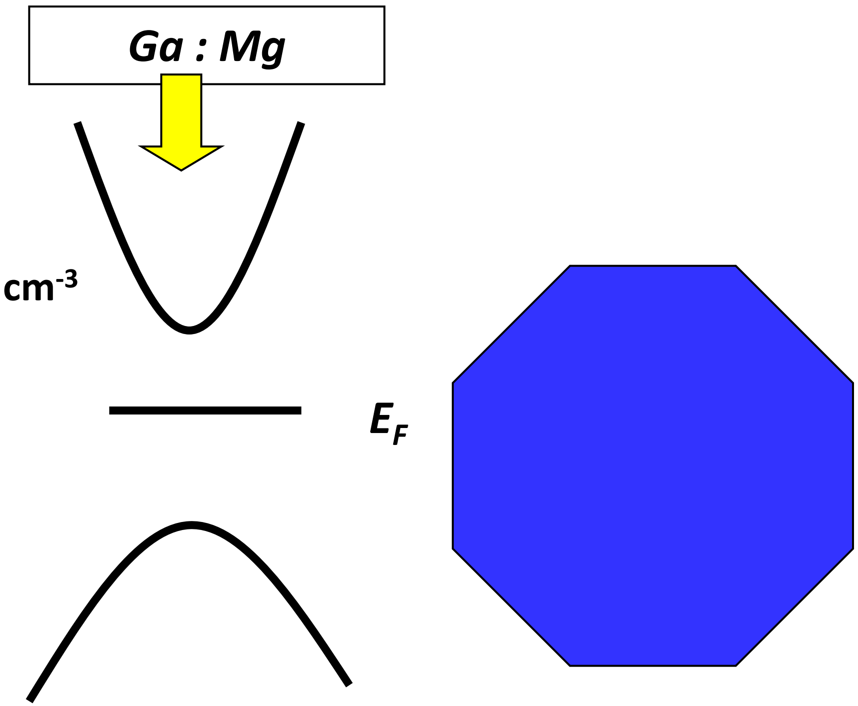


Perfect crystallographic quality but…too small!

I. Grzegory et al. in Bulk Crystal Growth of Electronic, Optical and Optoelectronic Materials, ed. by P. Capper, Wiley&Sons, (2005), 173

High Nitrogen Pressure Solution (HNPS)

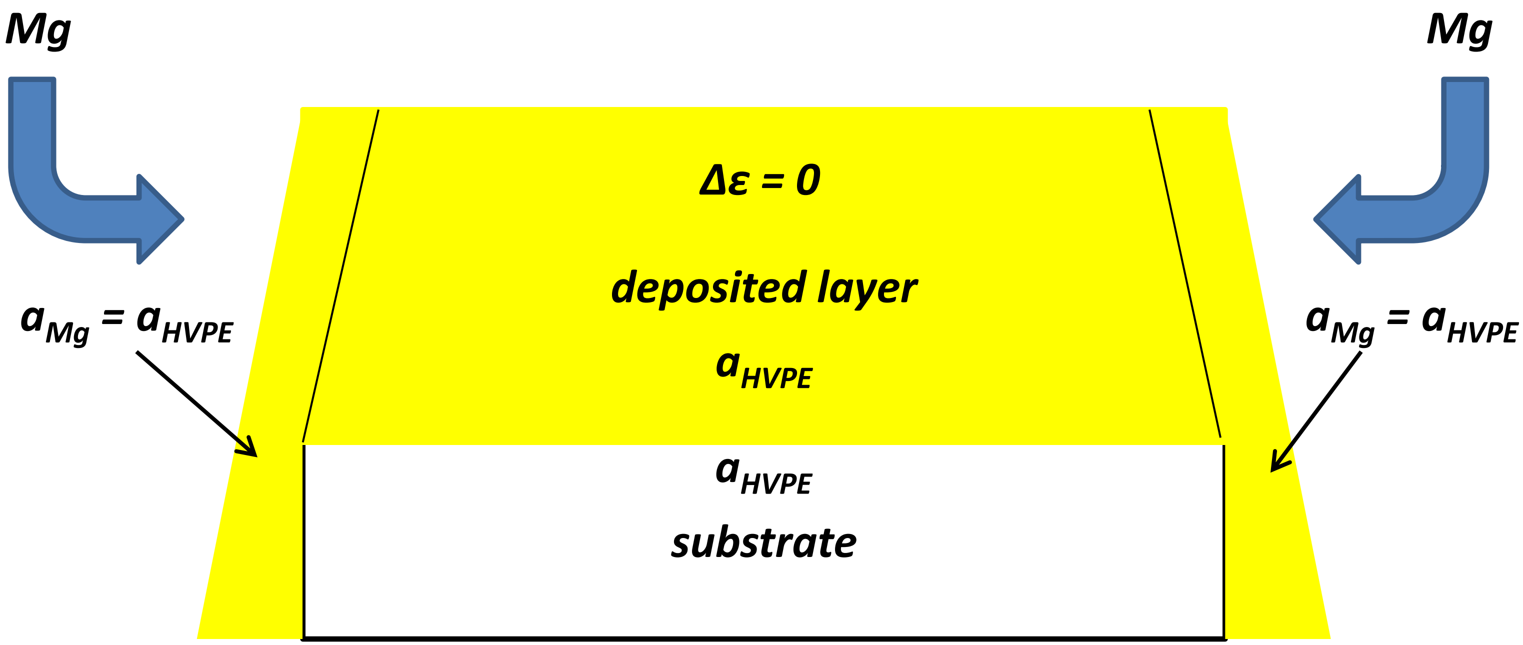




Compound	a (Å)	c (Å)
1. GaN undoped homoepitaxial layers (MOCVD)	3,1885±0.0003	5.1850 ±0.0001
2. Mg-doped bulk (low free electron concentration)	3,1885±0.0003	5.1850 ±0.0001
3. GaN bulk, free electron concentration $5x10^{19}$	3,1890±0.0003	5.1864 ±0.0001

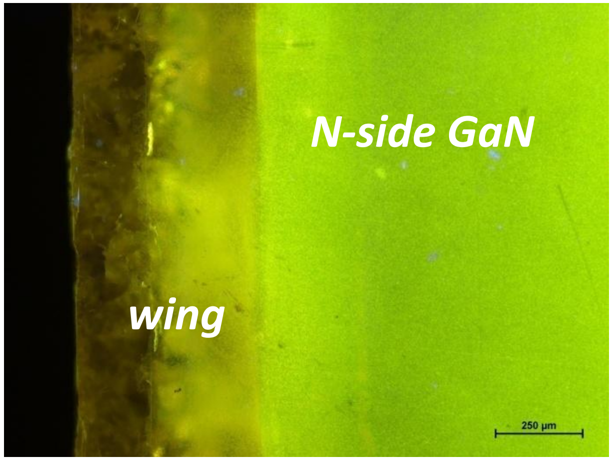
Potential solutions

Magnesium loves oxygen; oxygen loves magnesium!

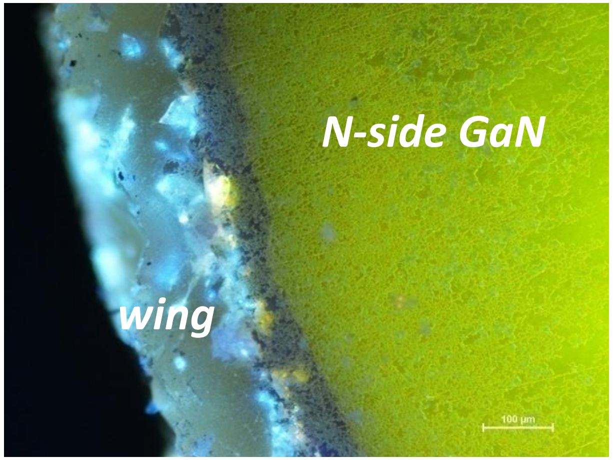


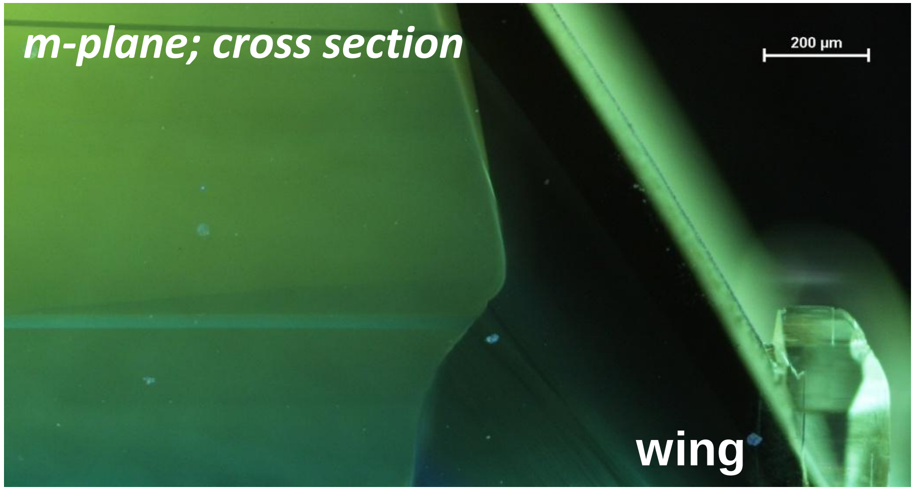
Potential solutions

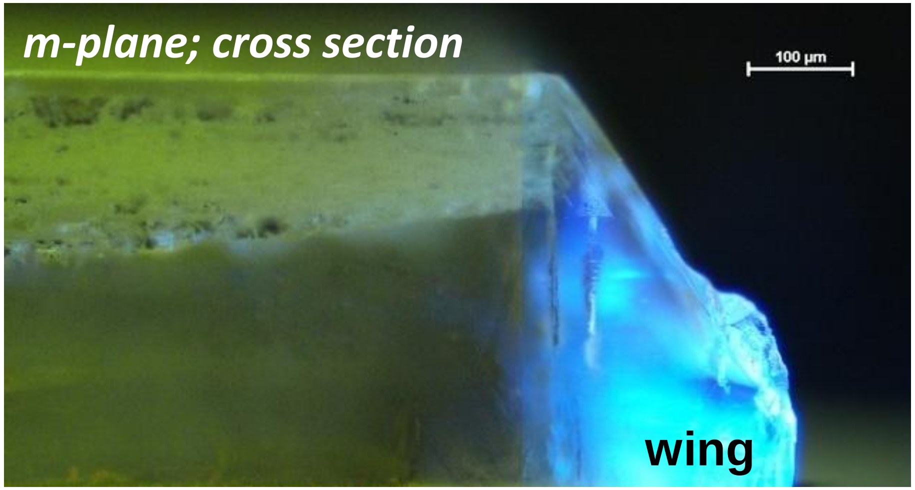
GaN



GaN:Mg

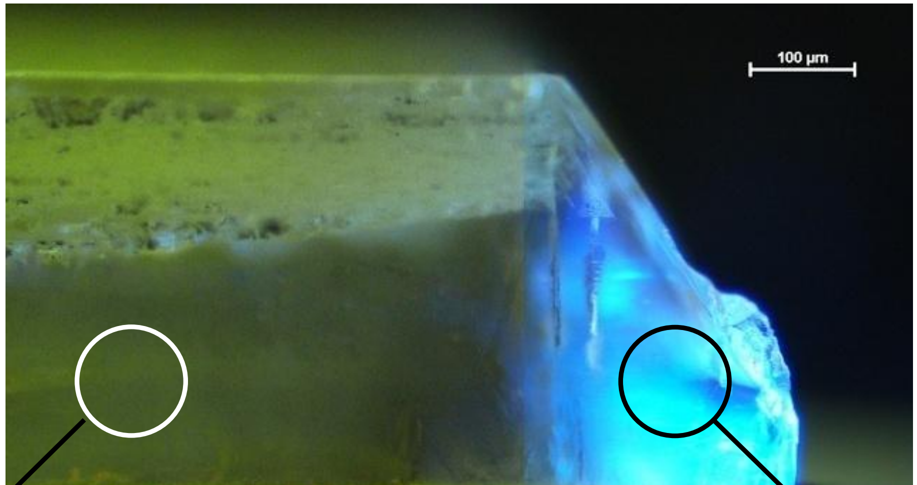


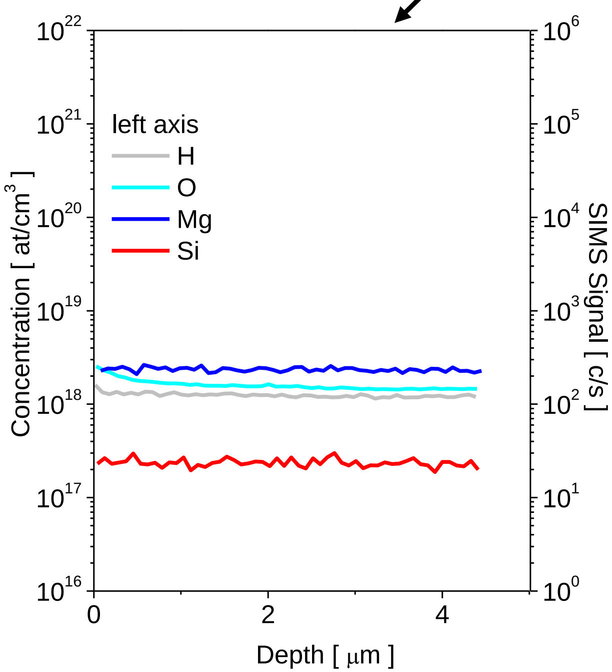


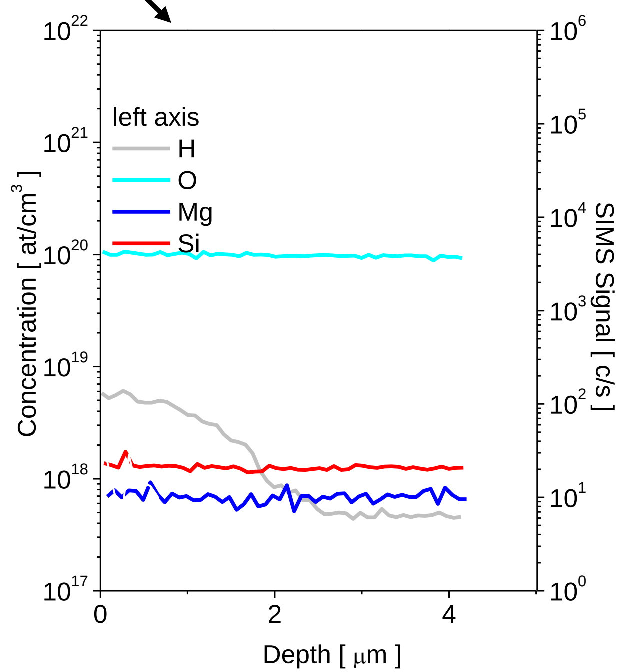


Potential solutions

SIMS



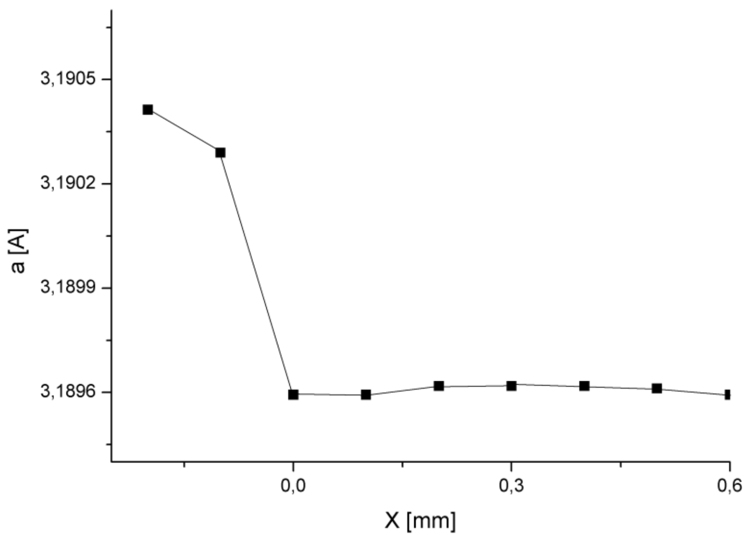




Potential solutions

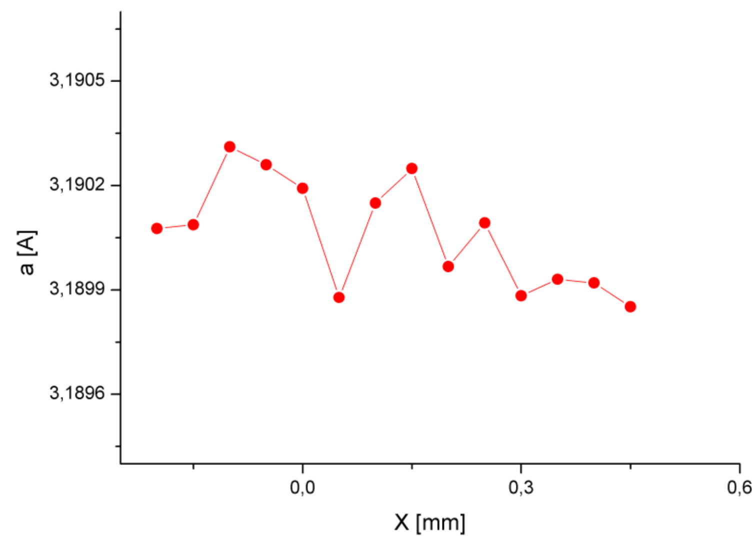
GaN vs GaN:Mg – lattice parameters

GaN



wing *c-plane layer*

GaN:Mg



wing *c-plane layer*

beam size: 0.04 mm x 0.1 mm

Summary

There are three GaN growth methods; today only one of them is applied for „GaN substrates mass production".

The main disadvantage of all GaN growth methods is anisotropy of the growth and growth in lateral direction.

Concentration of impurities as well as the types of impurities are different on c-plane and on non-polar and semi-polar facets. This causes stress in the growing crystal.

Lattice constants engineering should be introduced.

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