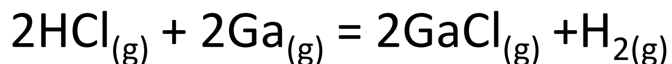
HVPE-GaN growth on ammonothermal GaN seeds:

State of the art

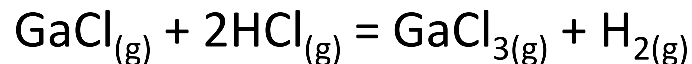
Influence of seed misorientation

Growth rate vs Critical Thickness

Background of the Halide Vapor Phase Epitaxy



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



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

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

Substrats zone T= 850°C

Growth zone T= 1045°C

$N_2/H_2 + HCl$

Ga

$H_2/H_2 + GaCl$

$N_2/H_2 + NH_3$

$N_2/H_2 + GaCl + NH_3$

Seed holder

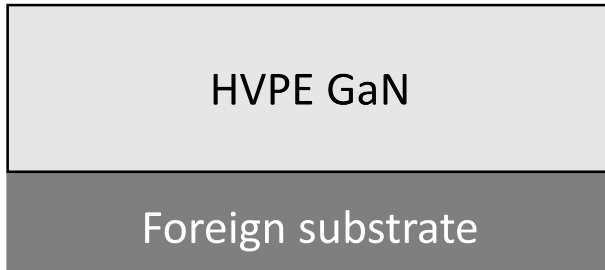
Carrier gas: N_2/H_2

$$\Delta P_{Ga} = [P^{\circ}_{GaCl} - (P_{GaCl_3} + P_{GaCl})] \quad \text{(nitrogen reach condition)}$$

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

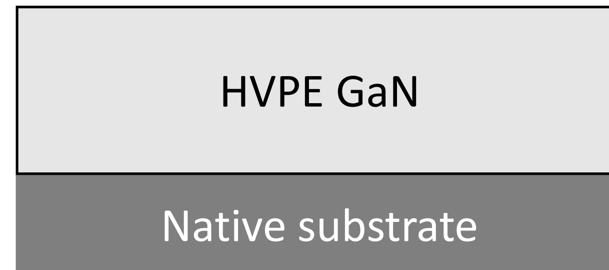
Seeds for HVPE growth

HETEROEPITAXY



Al_2O_3

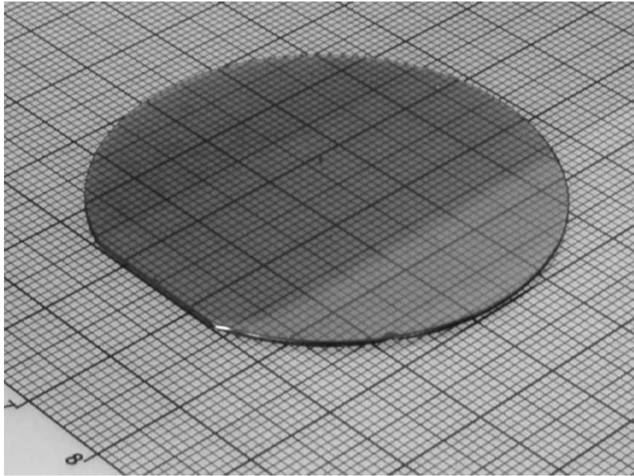
HOMOEPITAXY

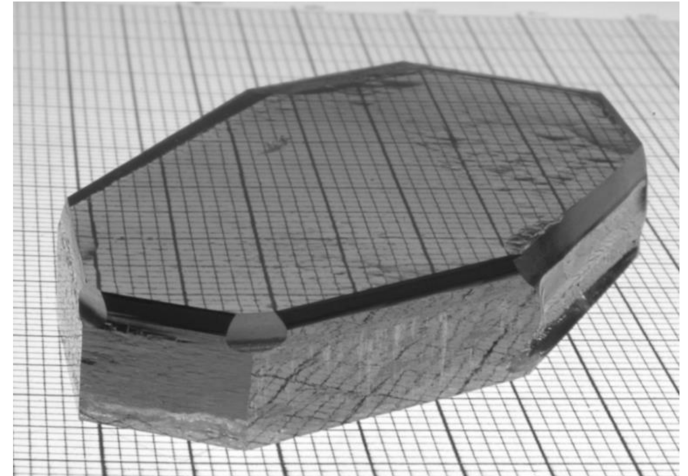


Ammono-GaN

Ammono-GaN crystals available on market

ammono

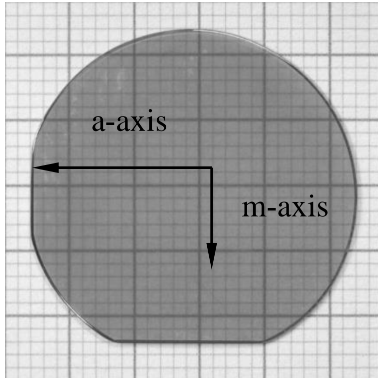


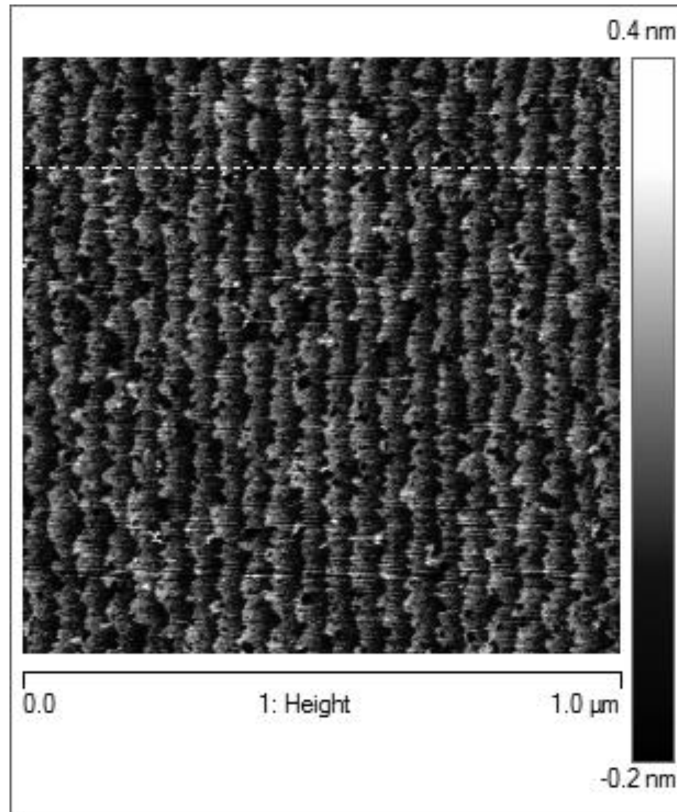


- **TDD ≈ 10^4 cm^{-2}**
- **R > 20 m (even > 100 m)**
- FWHM of XRC = 18 arcsec*
- Growth rate ≤ 10 μm/h
- Carrier concentration: n-type, p-type, semi-insulating

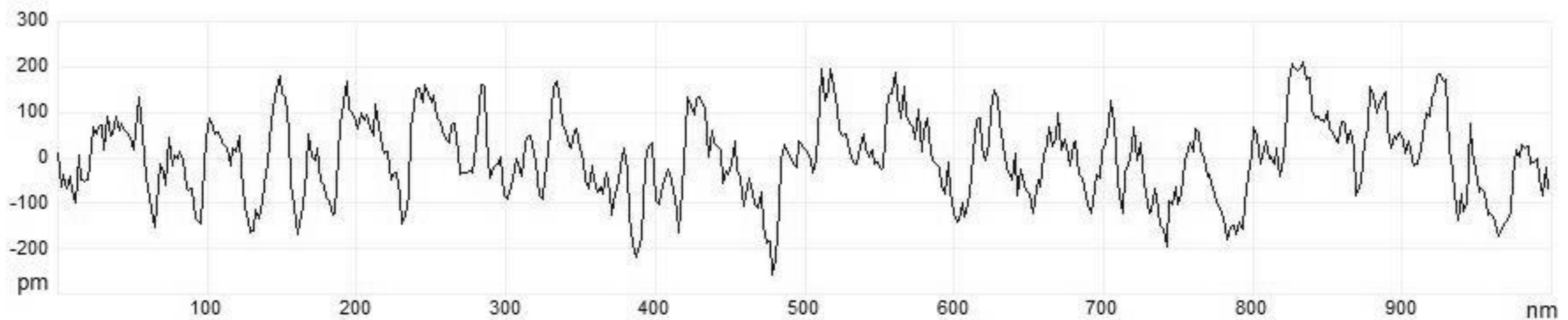
* beam size = 0.1×0.1 mm^2

Seeds preparation to epi-ready state

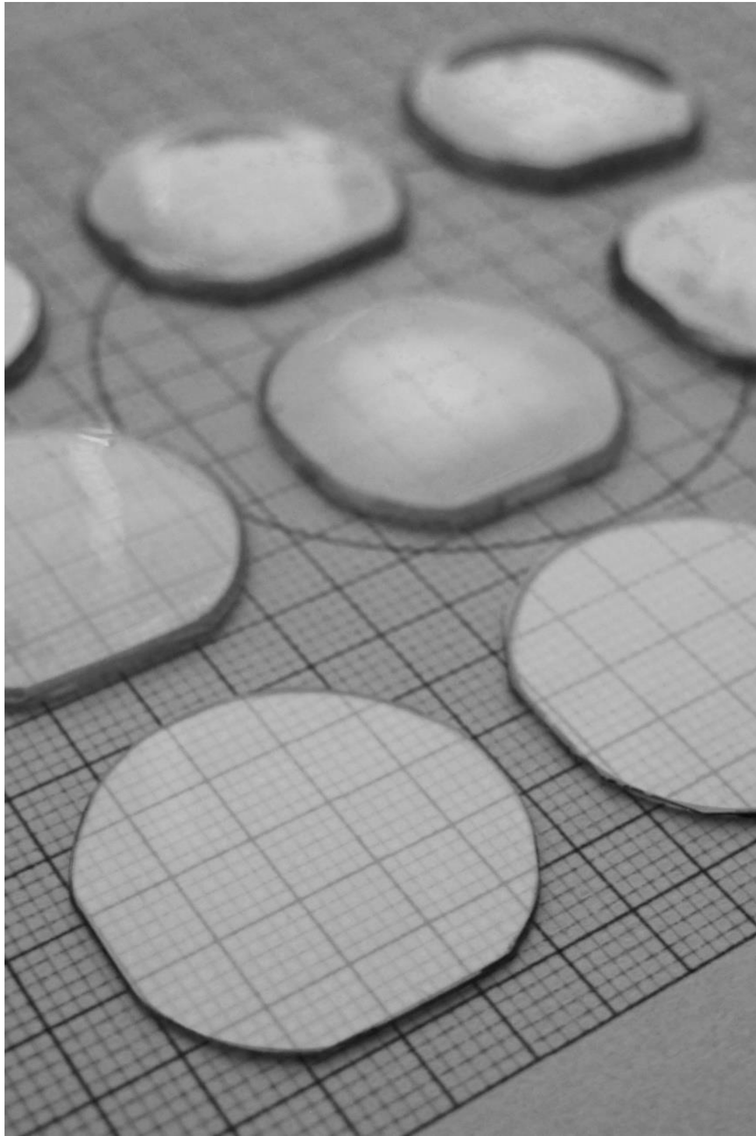




- Mechano-chemical polishing
- RMS = 0.1 nm
- Visible atomic steps
- FWHM of XRC was improved



HVPE-GaN layers grown on 1-inch Am-GaN seeds

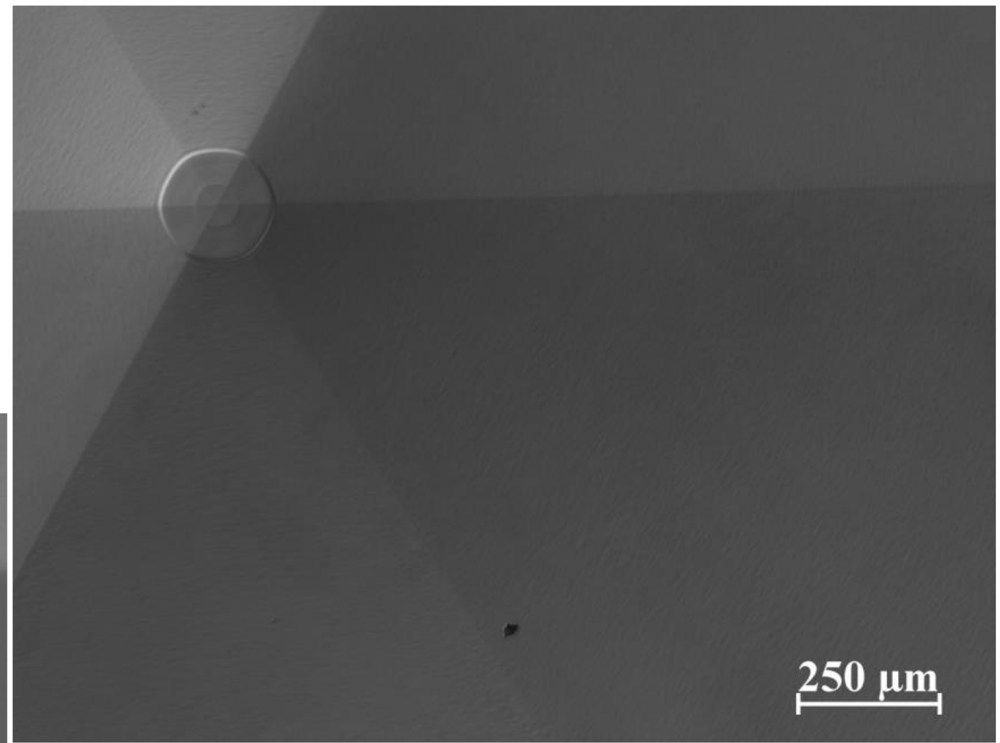


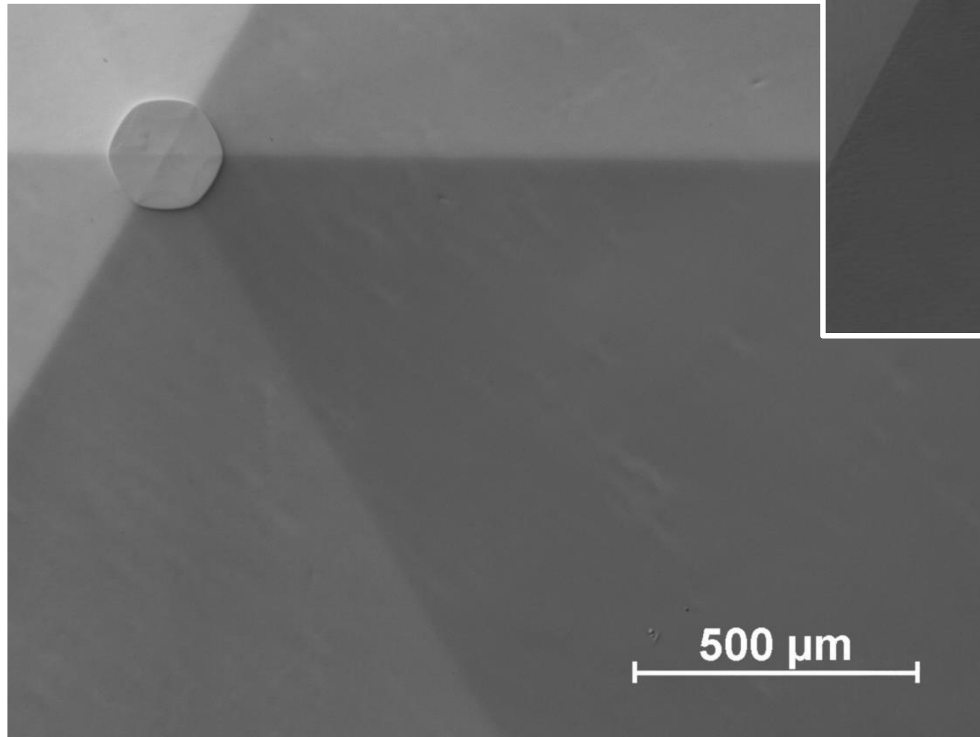
- Seed misorientation: 0.3° to m direction
- Seeds with n= $5x10^{17}$ - $5x10^{18}$ cm^{-2}
- **Size: 1 inch**

- Growth temperature: 1050°C
- V/III ratio: 20
- H_2 as a carrier gas
- Crystallization time: 7 – 9 h
- **Growth rate: 150-330 µm/h**

Surface morphology of HVPE-GaN grown on Ammono-GaN

After 8h of growth





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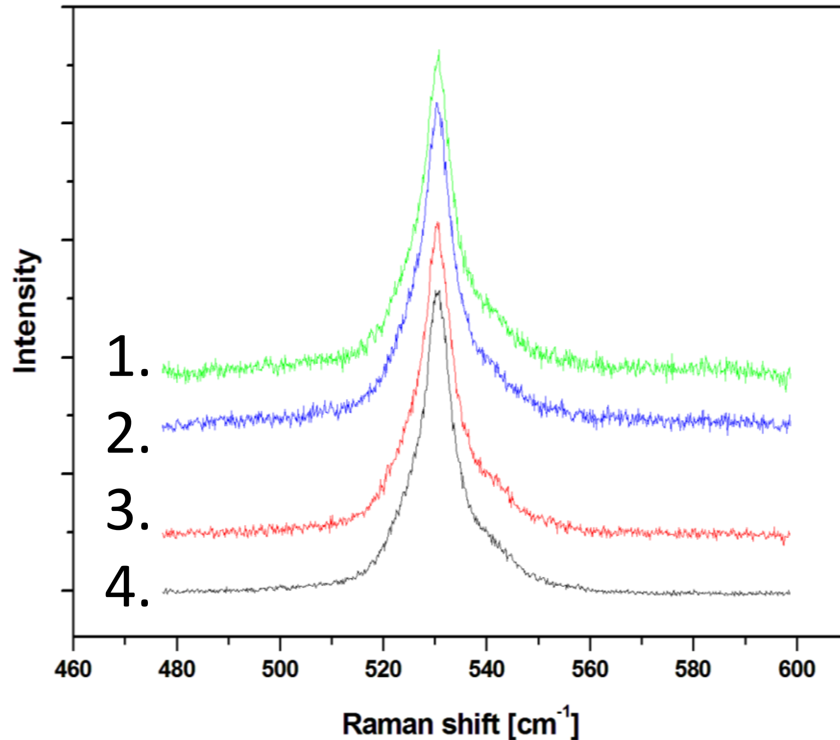
Scanning Raman spectra through the cross section



Scanning Raman spectra through a cross-section (m-plane) of an HVPE-GaN/Am GaN couple.

No shift of the A1(TO) peak is observed for the HVPE-GaN and the Am-GaN seed; measurements were performed at different distances from the interface.

1. HVPE-GaN 600 µm above the interface
2. HVPE-GaN 200 µm above the interface
3. Am-GaN seed 200 µm below the interface
4. Am-GaN seed 600 µm below the interface

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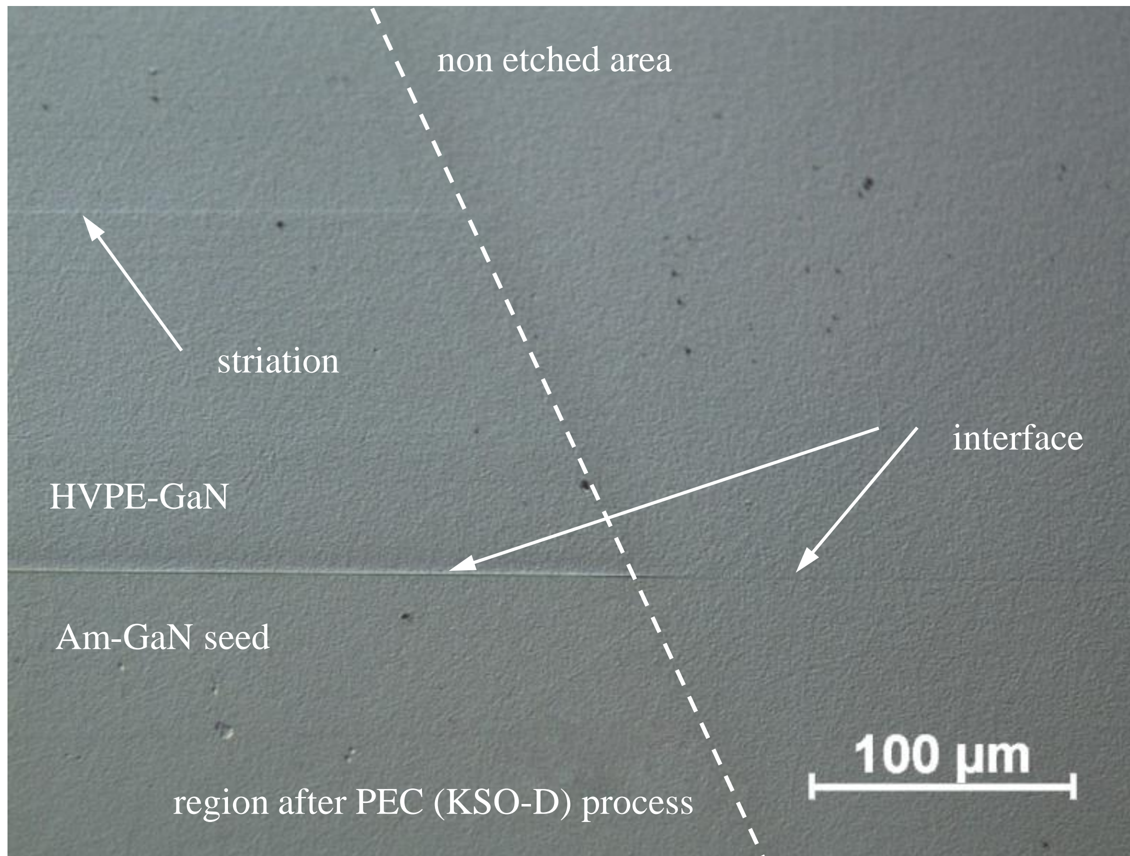
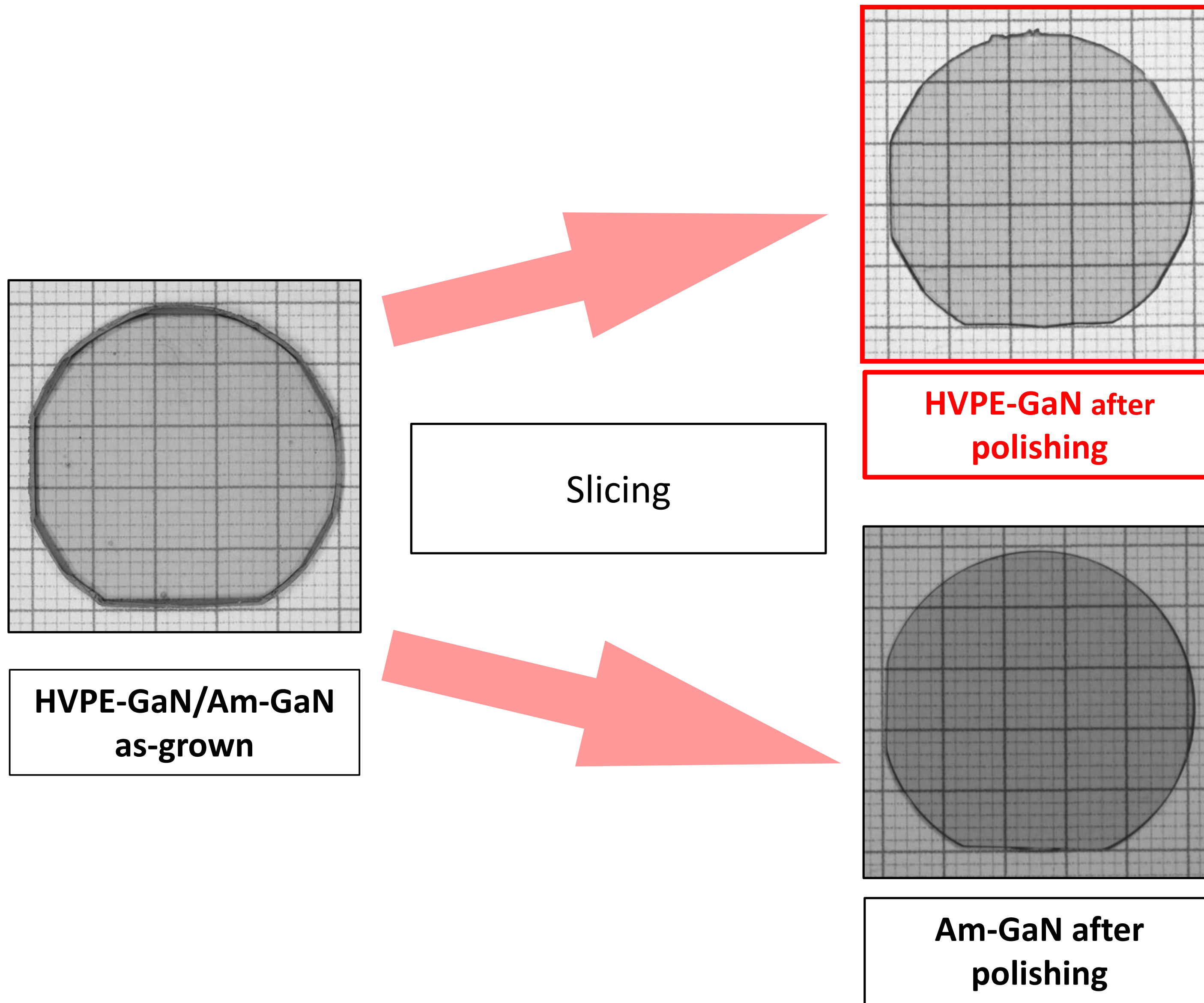
Cross-section (cleaved in m plane) of HVPEGaN/Am-GaN couple



Materials above the interface and below it seemed homogeneous. Some striations could be found in the HVPE-GaN. One of them is marked. It should be noticed that the features such as interface and/or striations were not well visible in the non-photo-etched region.

Free-standing HVPE-GaN from Ammono-GaN



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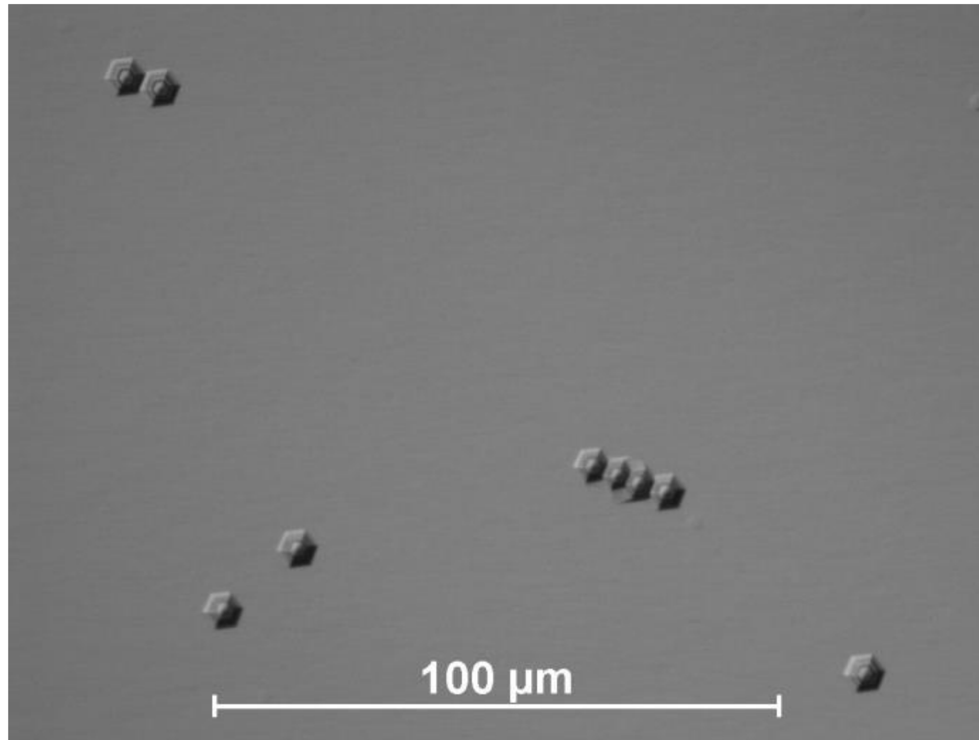
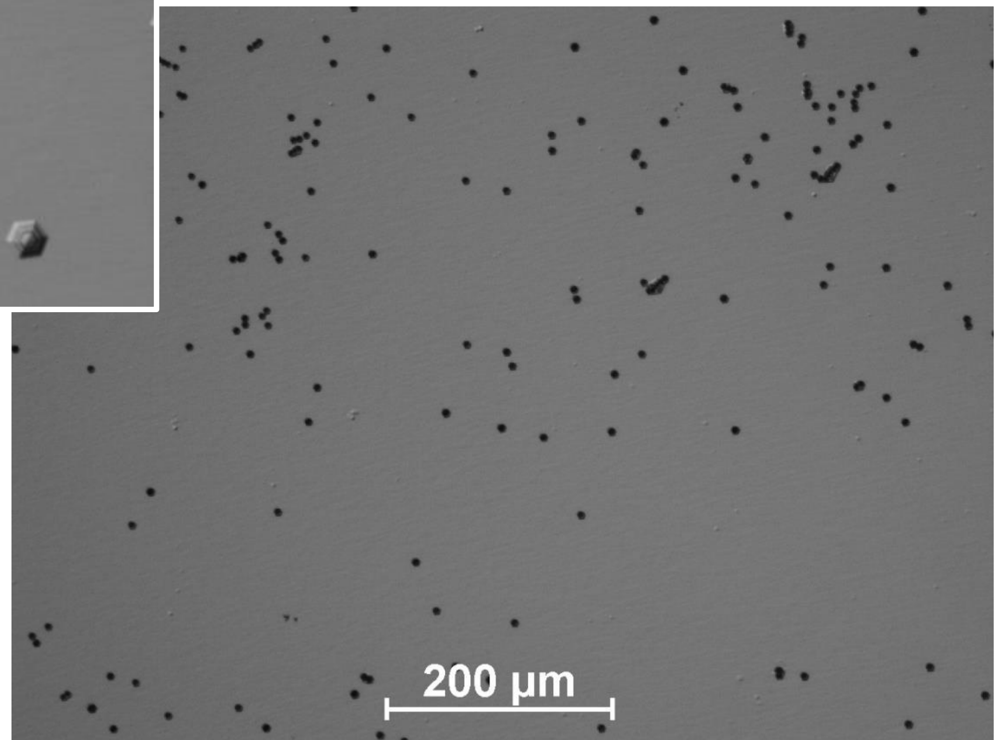
HVPE-GaN grown on Ammono-GaN – dislocation density

molten KOH/NaOH 450 ^{o}C



TDD = $4x10^{4}$ cm^{-2}



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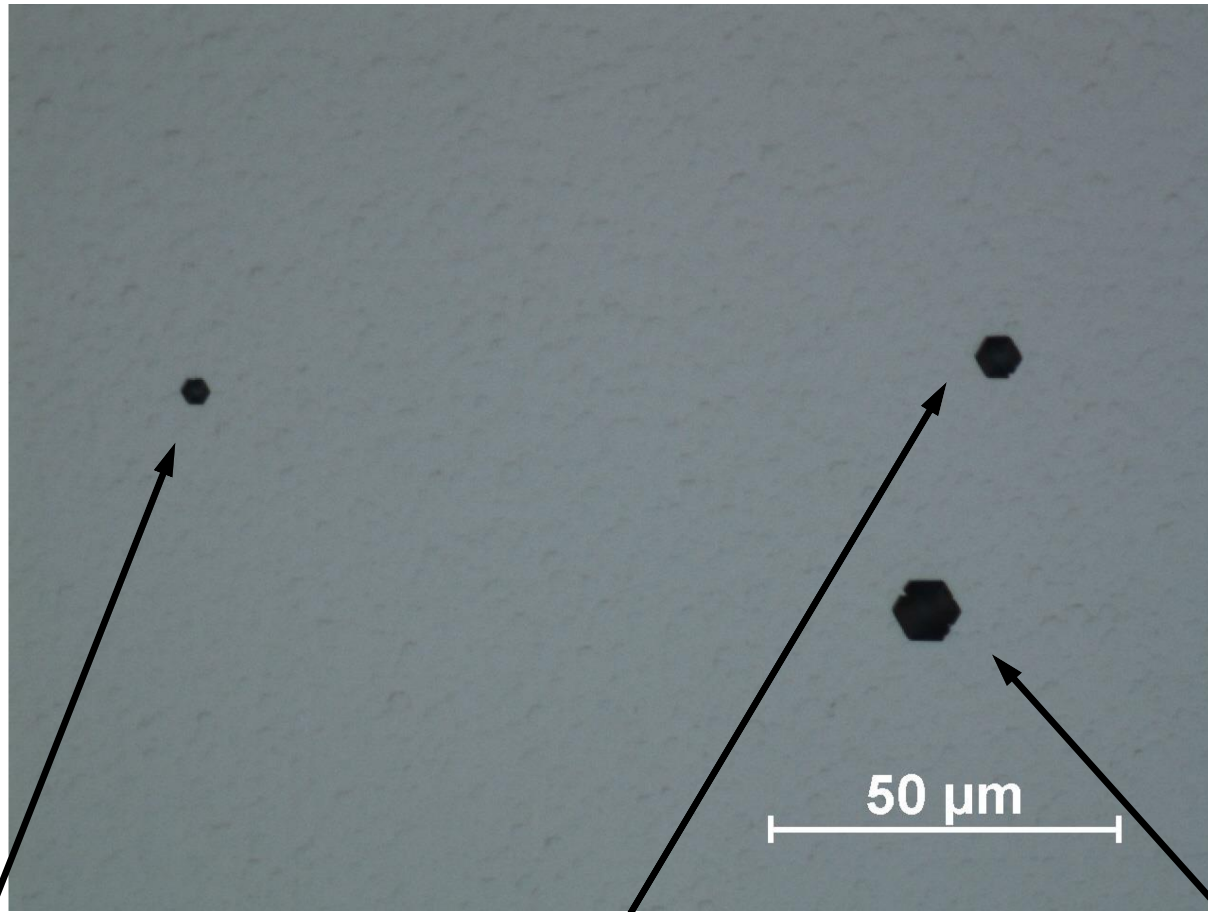
Types of dislocations revealed by DSE



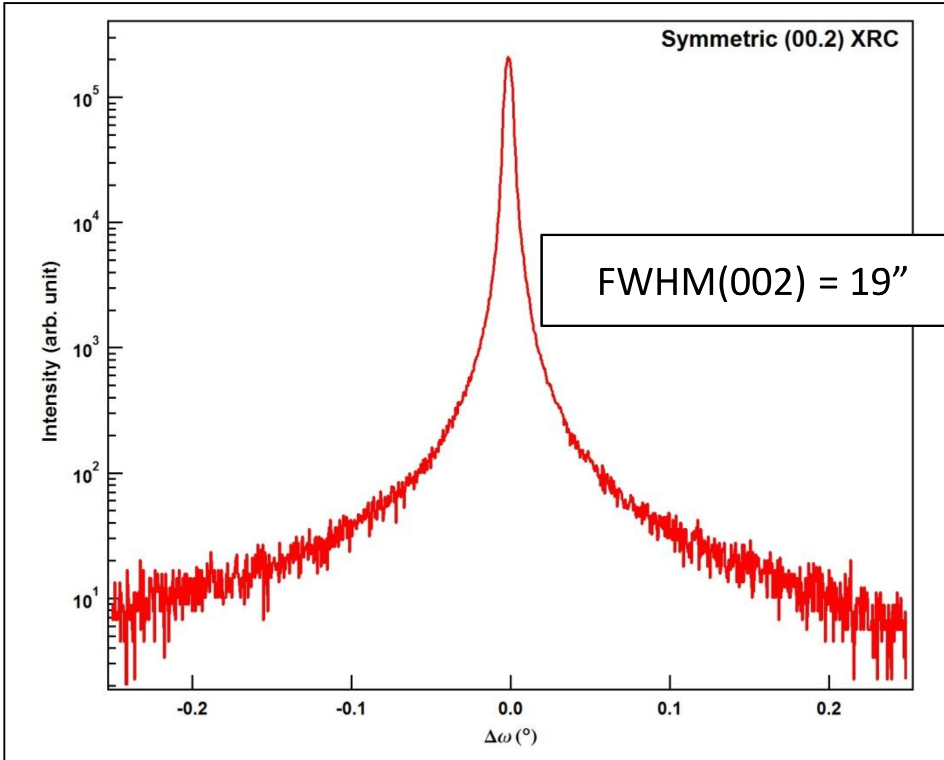
molten
KOH/NaOH
450°C

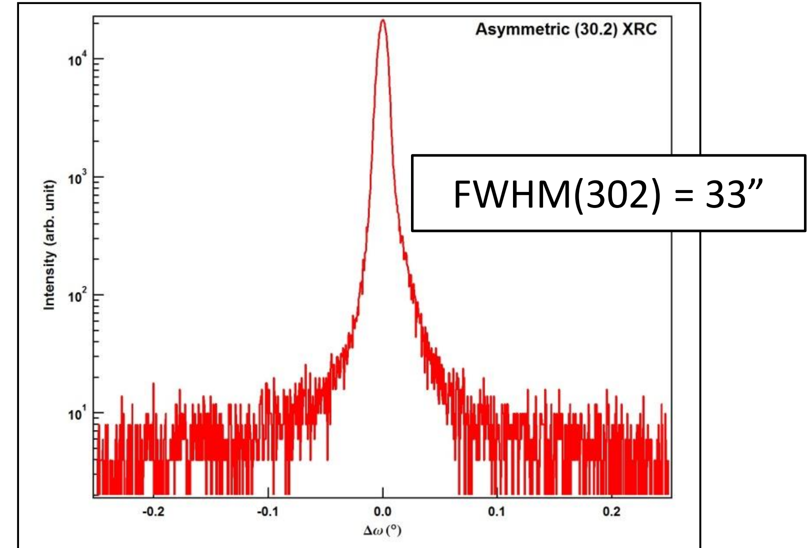
Edge dislocation

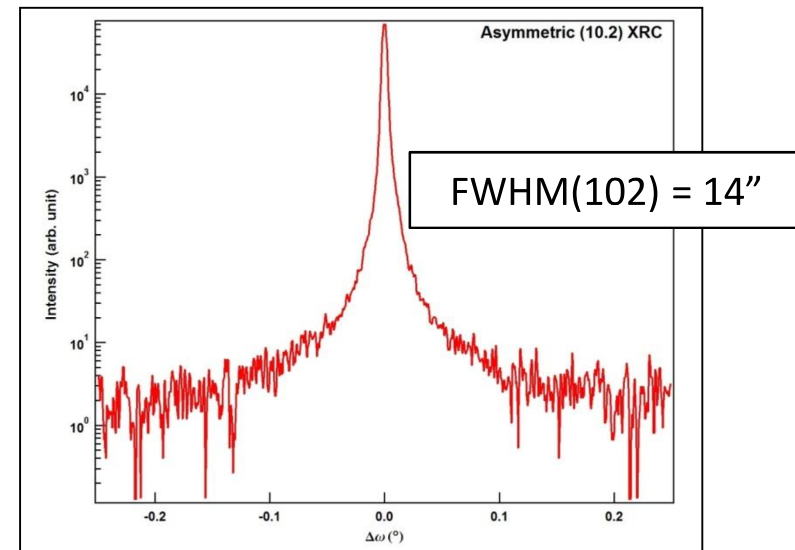
Mixed dislocation

Screw dislocation

Structural Quality – free-standing HVPE GaN



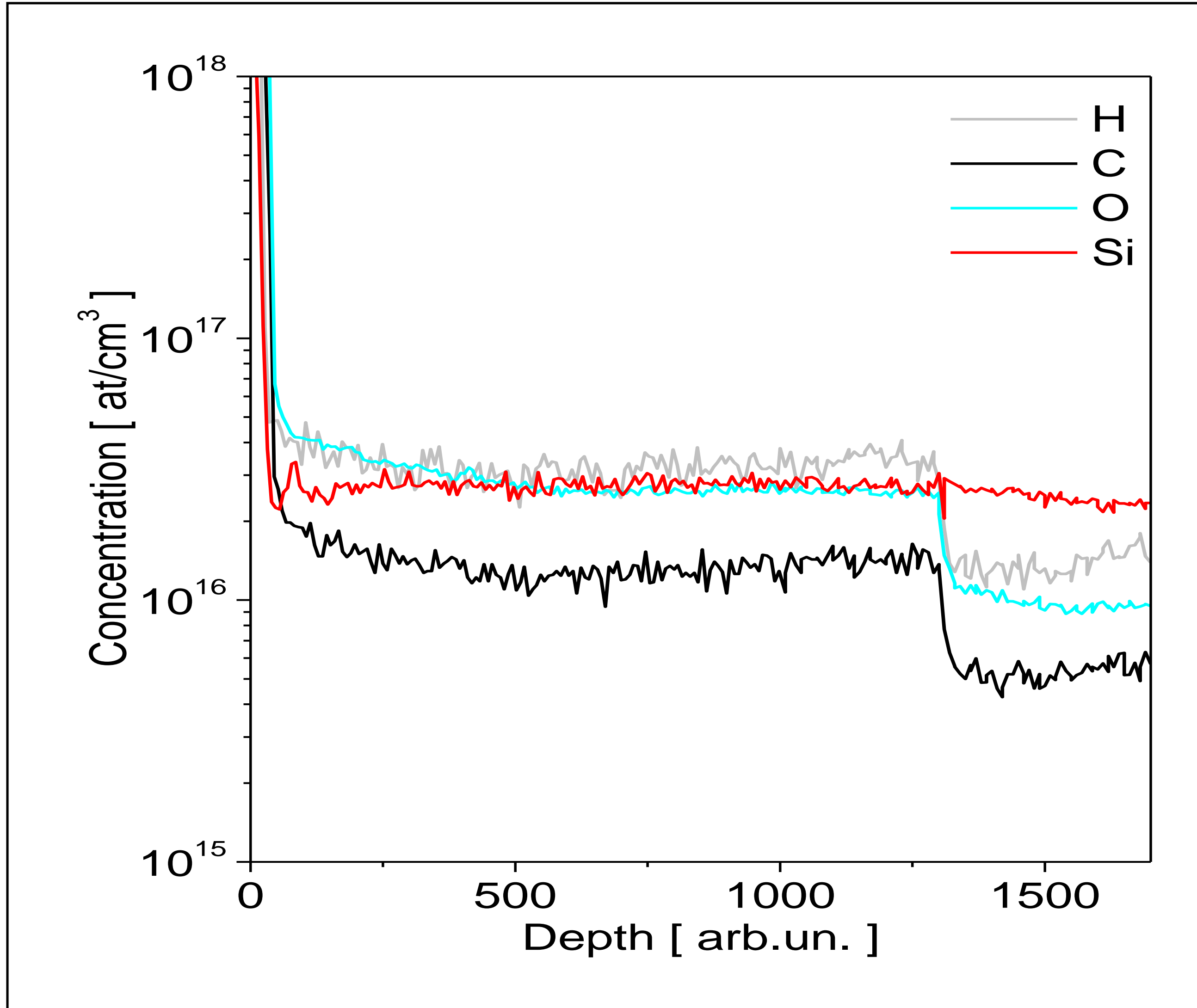




Thickness = 330 µm

R > 10 m

Purity - SIMS measurements



Below detection limit

H: $1x10^{16}$ cm^{-3}

C: $5x10^{15}$ cm^{-3}

O: $9x10^{15}$ cm^{-3}

Real value

Si: $3x10^{16}cm^{-3}$

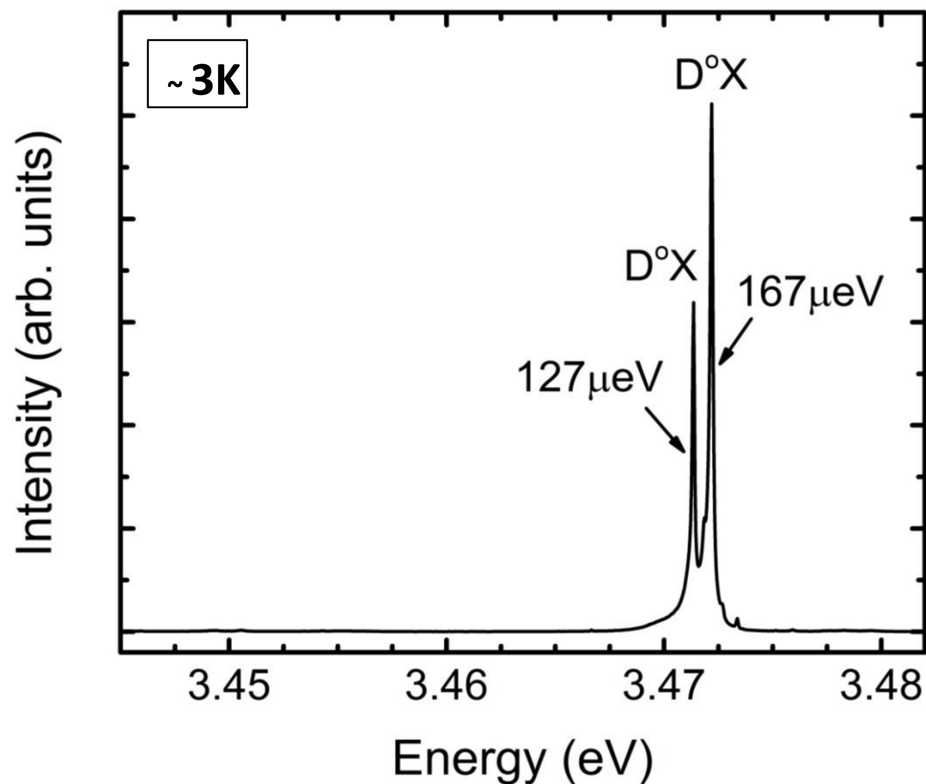
Electrical properties

n= $1.7x10^{16}$ cm^{-3}

μ=1120 $cm^2/V\cdot s$

Optical quality – low-temperature photoluminescence of F-S HVPE-GaN

Two sharp donor bound exciton emission lines at 3.471 eV and 3.472 eV



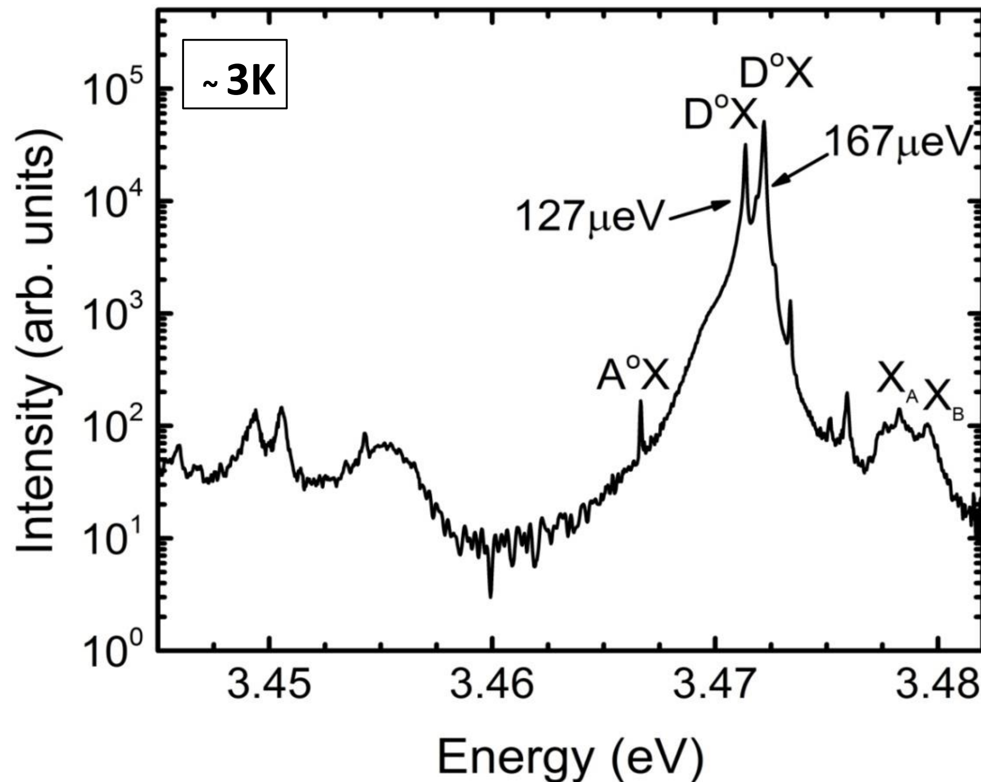
He-Cd laser
(λ~325 nm)

Closed-cycle Helium cryostat,

Princeton Instruments Acton SP2750 0.75 m high-resolution monochromator with 3600 grooves/mm grating,

PIXIS: 2KBUV cooled charge-coupled device camera

Free and bound exciton emissions confirm the high optical quality and purity.



acceptor bound exciton emission at 3.466 eV

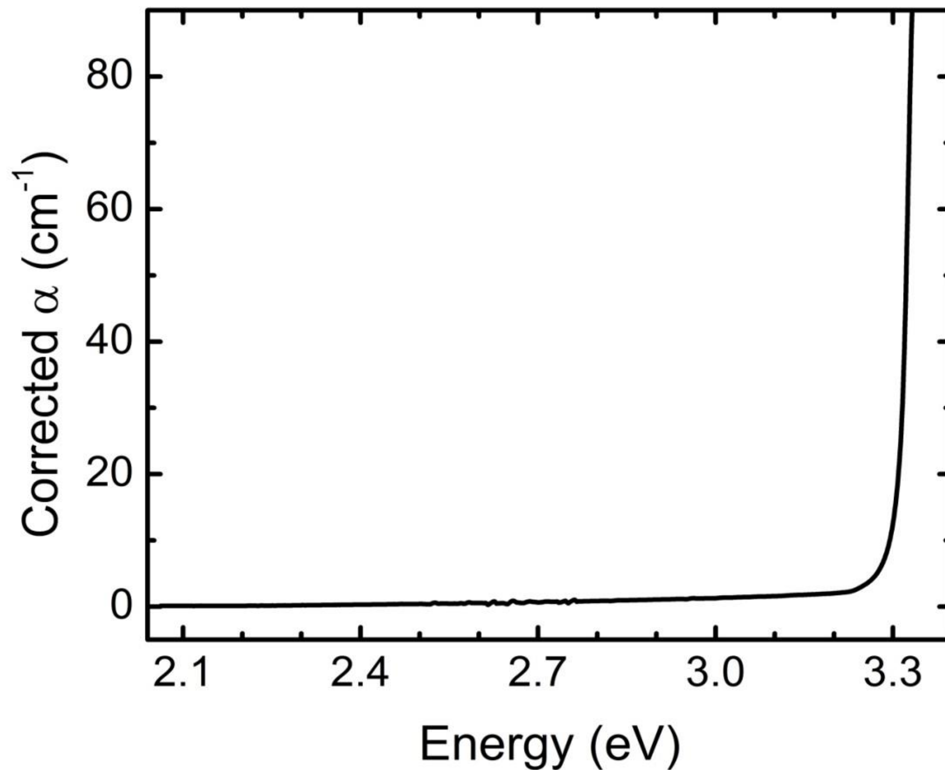
donor bound exciton emission at 3.471 eV and 3.472eV

free exciton emissions at 3.478 eV and 3.480 eV

very weak and broad yellow-green luminescence

Optical quality – room-temperature transmission – F-S HVPE-GaN

No structure was observed in the absorption spectra close to the band edge.

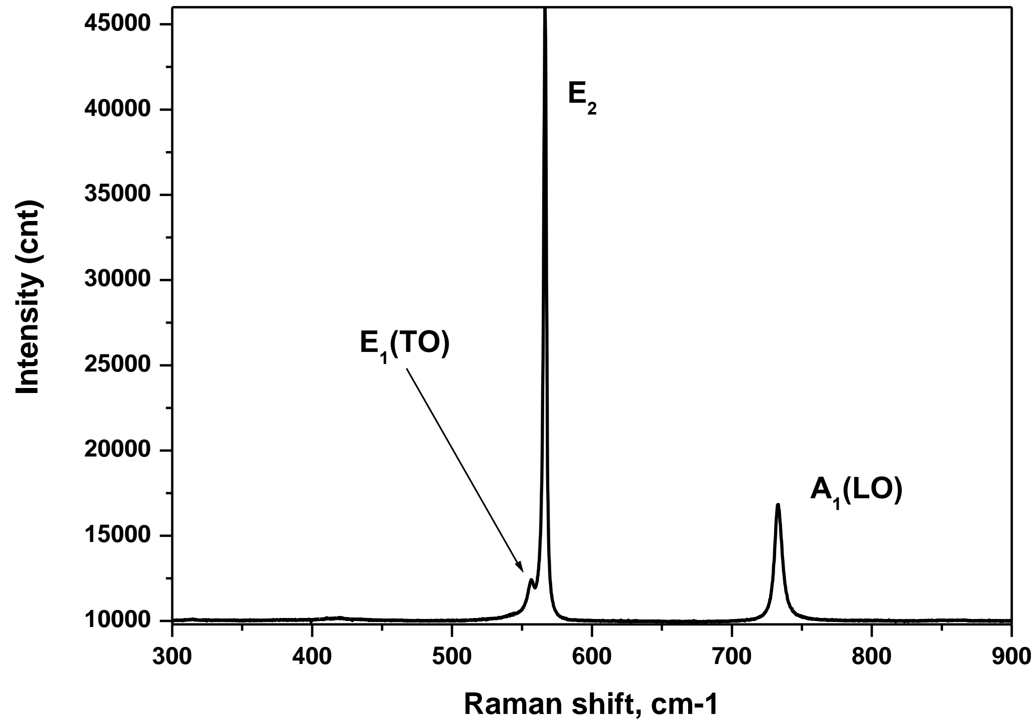


Hg(Xe) arc lamp source

Princeton Instruments Acton SP2750 0.75 m high-resolution monochromator with 3600 grooves/mm grating,

Free-standing HVPE-GaN - Raman spectrum

parallel to (0001) direction



	A1(TO)	E1(TO)	**E2**	A1(LO)	QLO
V. Darakchieva	530,6±0,1	557,9±0,1	**567,0±0,2**	733,6±0,1	740,3±0,1
A.R. Goni	531,7±0,3	558,2±0,1	**567,0±0,1**	736,5±0,2	742±0,2
c-GaN		556,5±0,5	**566,5±0,5**	733,0±0,5	

V. Darakchieva et al. in Nitrides with Nonpolar Surfaces, Wiley-VCH, (2008)
A.R. Goni et al. Physical Review B, 64, 035205 (2001)

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