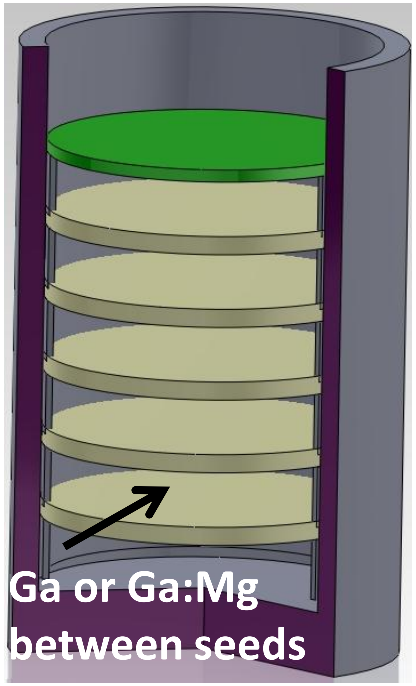
High Nitrogen Pressure Solution (HNPS) growth method

Seeded Growth
LPE Growth – The Multi Feed Seed Configuration

This configuration is based on the conversion of free-standing HVPE-GaN crystals to free-standing, pressure grown HNPS-GaN of a much higher quality than the seeds. The great strength of this approach is that it yields several GaN crystals from one run. What's more, the crystals satisfy all the criteria for being substrates.

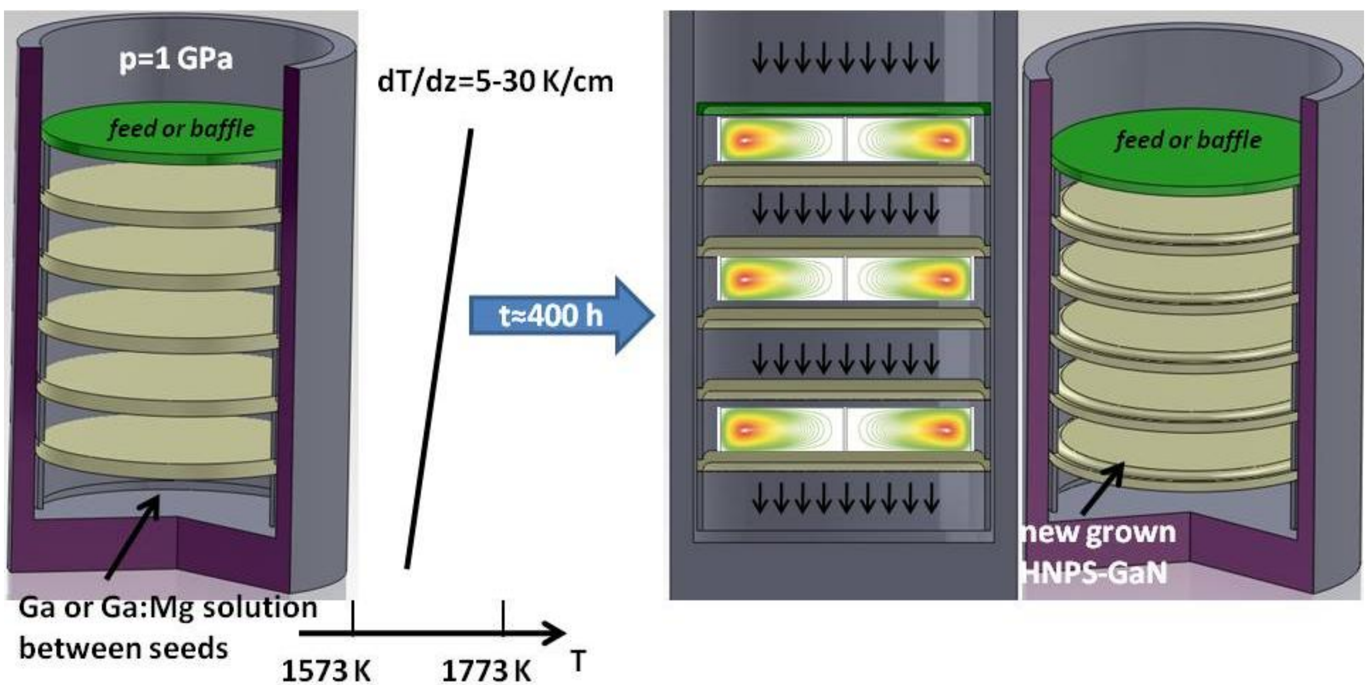
The production of this material begins with positioning several (0001) or (000-1) oriented HVPE-GaN seeds in a vertical stack, separated by liquid gallium or liquid gallium doped with magnesium, respectively.
The lowest seed is placed above the bottom of the crucible and the distance between individual seeds can be varied.



Seeded Growth

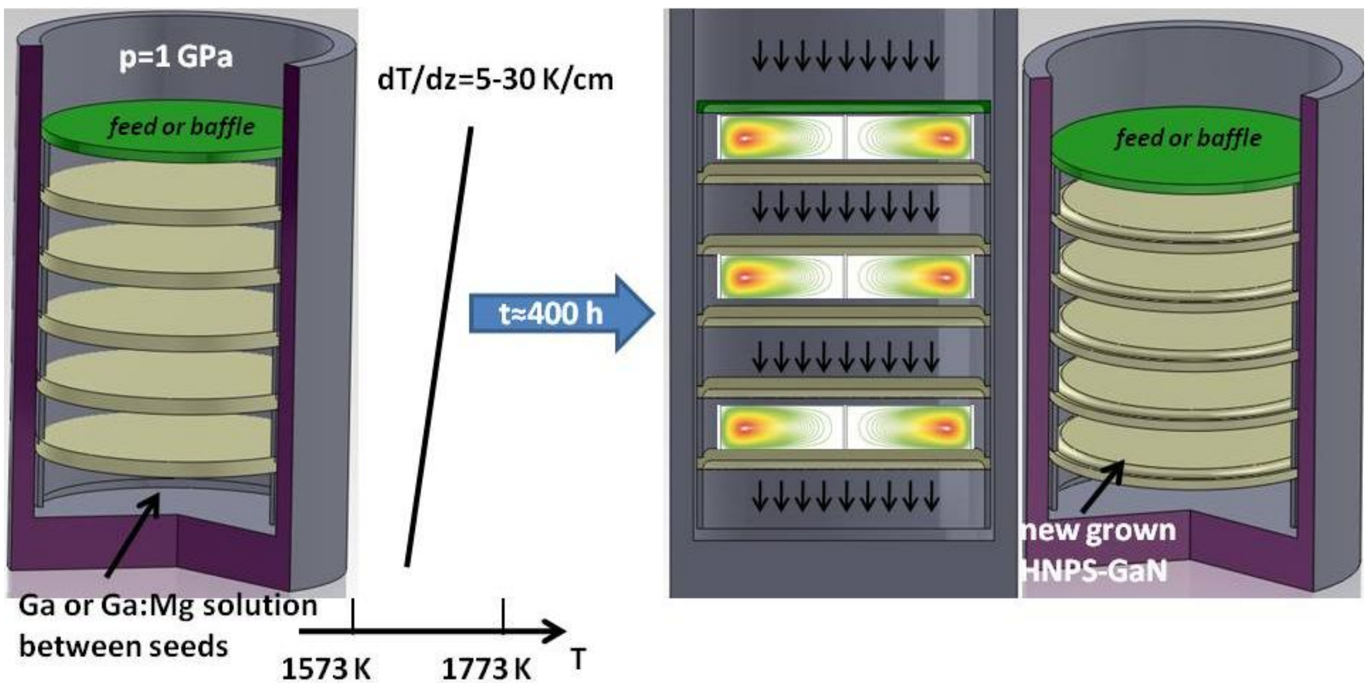
LPE Growth – The Multi Feed Seed Configuration

Under nitrogen pressure of typically 1 GPa and at a temperature of the level of 1593 - 1773 K, an axial temperature gradient (from 5 to 30 K/cm) is applied along the crucible. This leads to an overgrowth of seeds on their upper surfaces and the dissolution of the seeds on their opposite sides.



Seeded Growth
LPE Growth – The Multi Feed Seed Configuration

Due to the dissolution process, atomic nitrogen is supplied into the metal solution and is transported to the underlying crystal.
Each seed is overgrown and dissolved at the same time, but at slightly different temperatures, varying of about a few degrees. Therefore, they are feeds as well as seeds at the same time and the liquid gallium discs (sometimes doped by magnesium) play the role of traveling zones.



Seeded Growth
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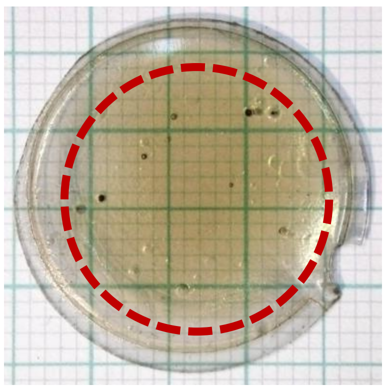
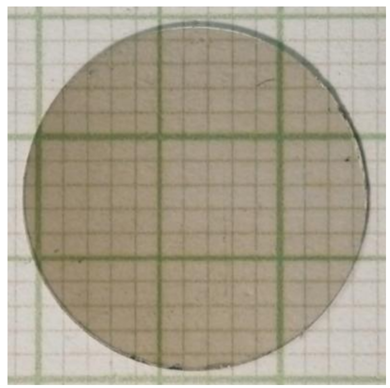
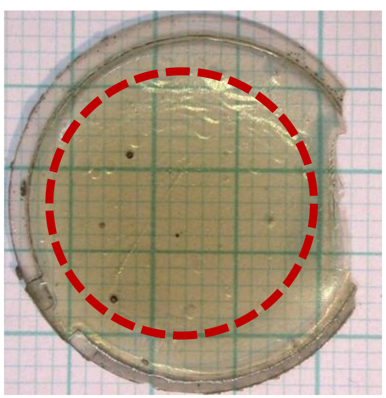
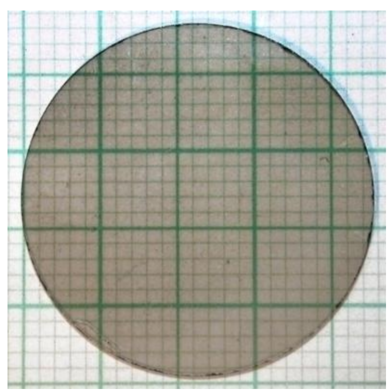
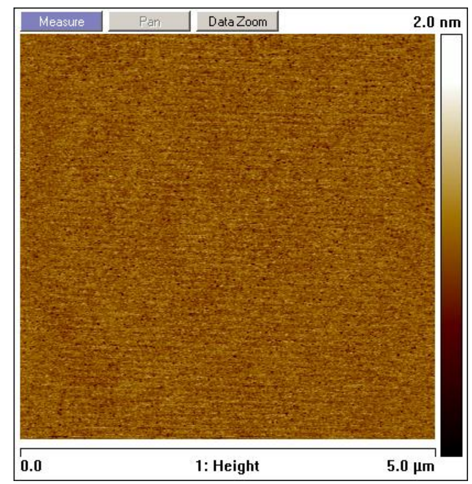
After the growth run (typically 400 h), the crystals are cut by a drill pipe to round forms of a diameter of 16 mm, 20 mm, 1 inch, or 1.5 inch. Then, their (0001) surface is mechanically and mechanochemically polished to the epi-ready state.







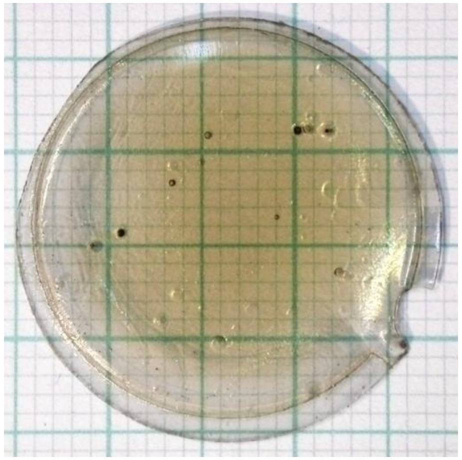


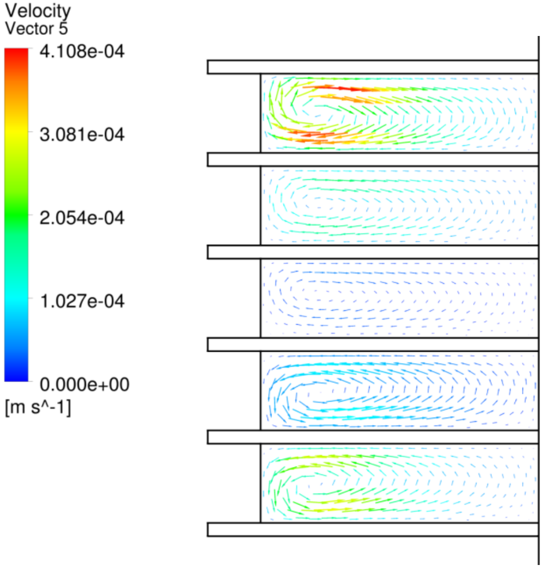


Seeded Growth
LPE Growth – The Multi Feed Seed Configuration

The HNPS growth in the MFS configuration results in a stable and macroscopically flat crystallization. This is associated with an appropriate convective or diffusive transport (flow) in the solution.

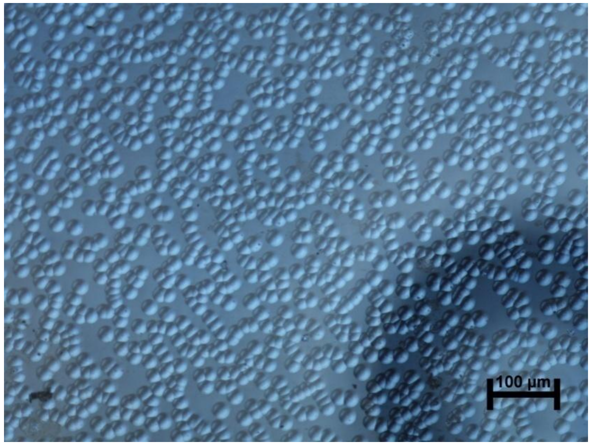
In the MFS configuration the gallium solution is divided by the HVPE-GaN seeds positioned in a vertical stack. The flow between the seeds has to be stable, since the upper crystals work like baffles for the lower crystals and they not only supply nitrogen to the solution but also stabilize the flow. The upper crystals also introduce an order to the Ga-N solution and uniform the nitrogen concentration field at the crystal's growing surfaces. This phenomenon allows to obtain a flat crystallization front and a flat growth of GaN during a long time.



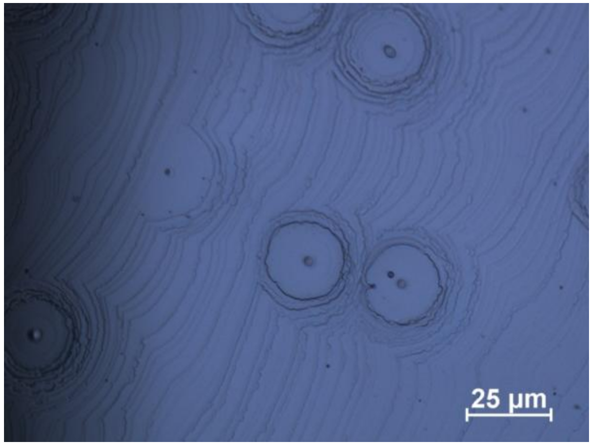


Seeded Growth
LPE Growth – The Multi Feed Seed Configuration

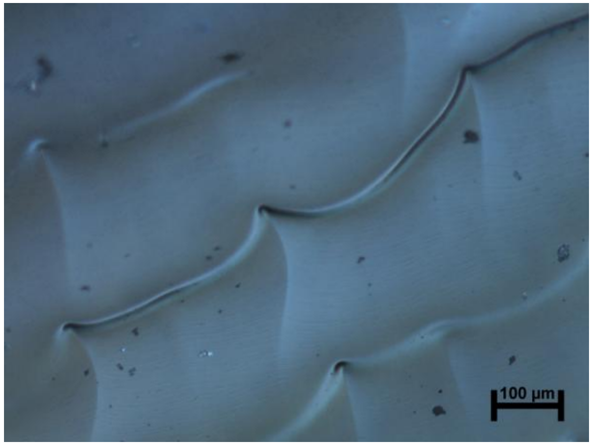
The HNPS crystallization in gallium without intentional doping always leads to n-type HNPS-GaN crystals. During the growth in the MFS configuration three types of morphologies are observed: hillocks, hillocks and macrosteps (mixed), and macrosteps.



hillocks



hillocks and macrosteps



macrosteps

Seeded Growth
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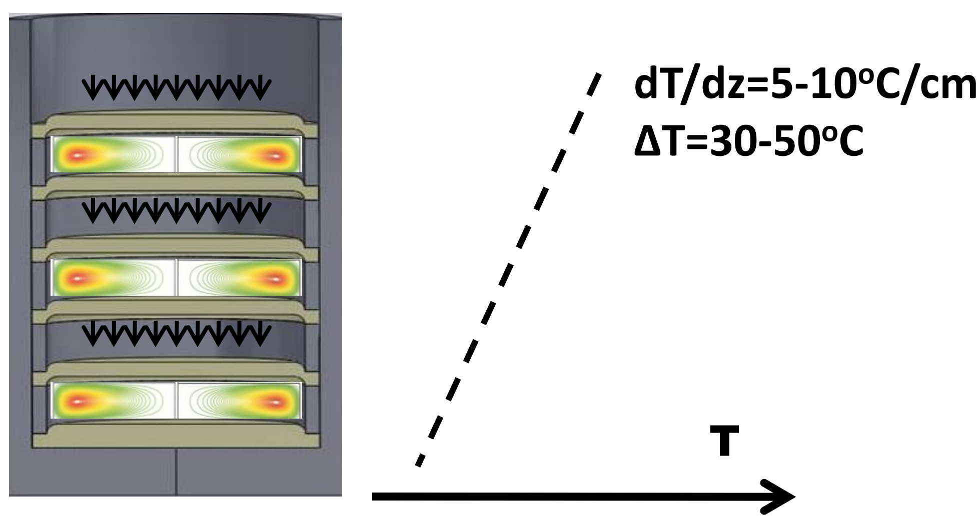
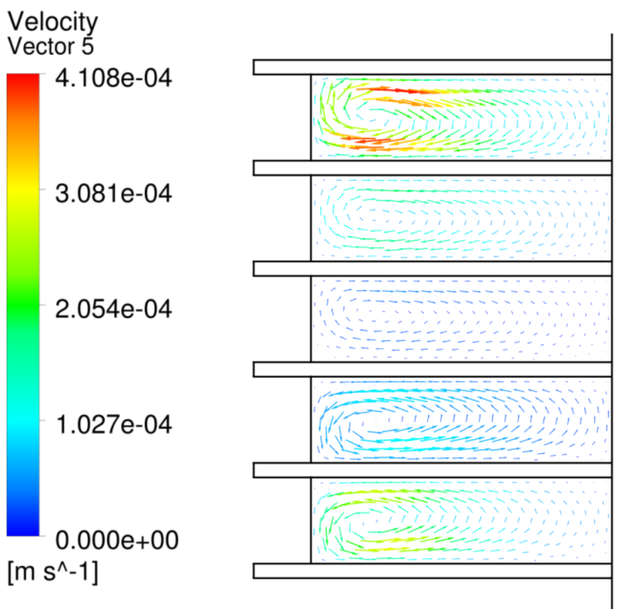
The presence of three modes of growth depends on the supersaturation at the growing crystal surface. The supersaturation mainly depends on the growth temperature, the temperature gradient applied, and the distance between seeds.
Since the growth temperature and gallium heights are fixed, the morphology of the grown crystal's surface depends only on the temperature gradient applied. Changing the temperature gradient varies the growth temperatures. It can be assumed that the system is still in a comparable temperature region.
The supersaturation is also associated to the mechanism of transport of nitrogen in the liquid gallium solution. The nitrogen can be transported by diffusion or convection from the upper to the lower seed.

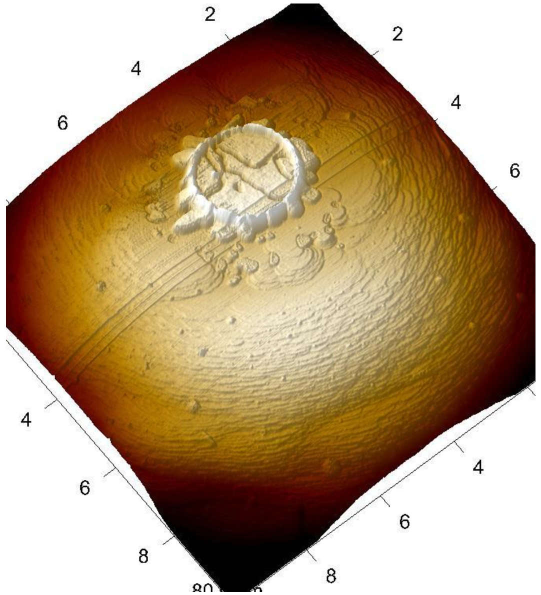


Seeded Growth
LPE Growth – The Multi Feed Seed Configuration

For the smallest temperature gradient (~5 K cm^{-1}) and low supersaturation, the hillock growth mode is observed. The growth rate is not higher than 1 μm/h. For the hillocks growth mode the diffusion of nitrogen in gallium plays a dominant role as the transport mechanism.

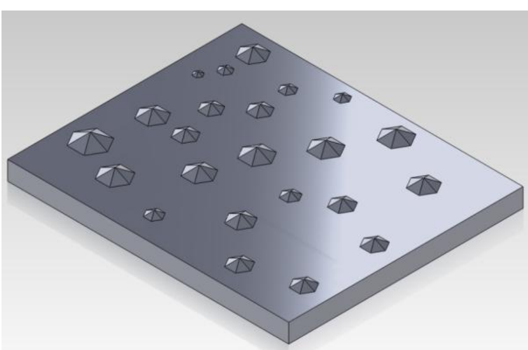
The hillocks growth mode is observed only for very low convectional velocities in gallium, of the order of 1×10^{-4} m s^{-1} or lower. Such small values of the calculated convectional velocities indicate a diffusive transport in the solution.

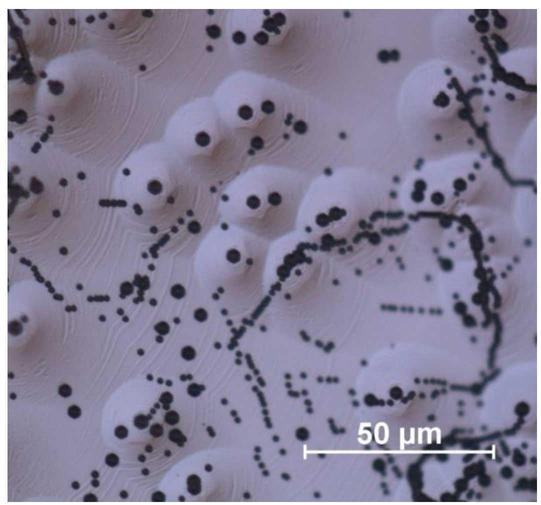


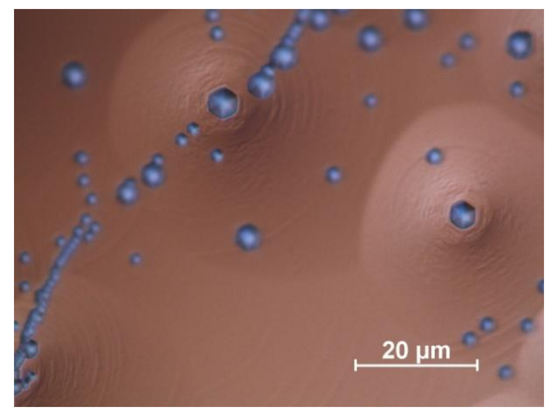


Seeded Growth
LPE Growth – The Multi Feed Seed Configuration

The hillocks are always correlated with screw and mixed dislocations in the pressure grown material. The big hexagonal etch pits, associated to the screw and/or mixed dislocations, are positioned on the top of each hillock. It should be noted that the hillock's density is always strictly the same as screw and mixed dislocation density in the HNPS-MFS-GaN, about 5 x 10^5 cm^{-2}.
The crystals are grown slowly by steps propagating from the hillocks' centers which are formed on the screw and mixed dislocations.

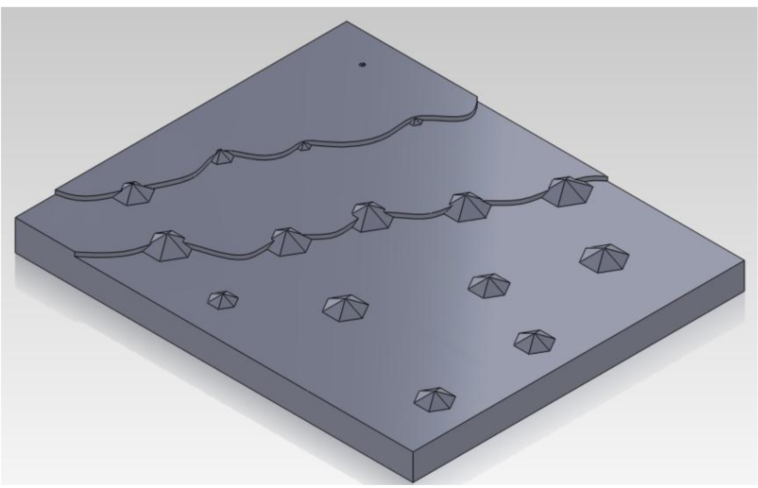


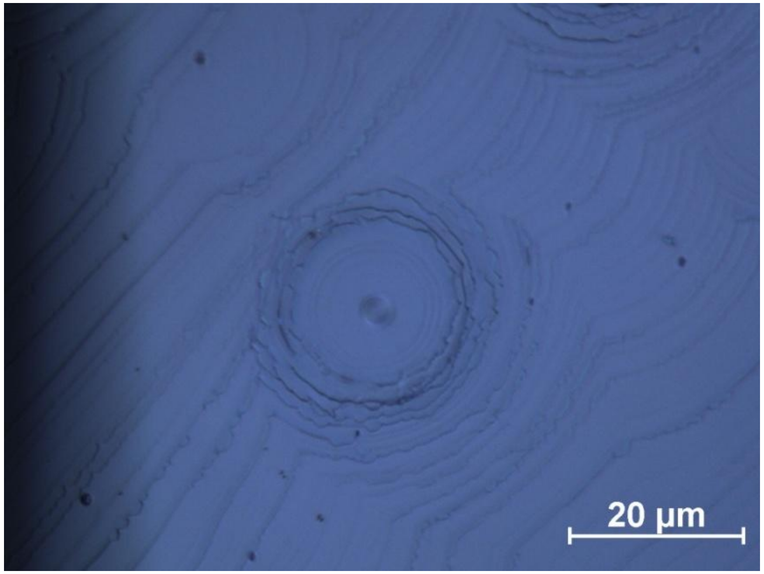




Seeded Growth
LPE Growth – The Multi Feed Seed Configuration

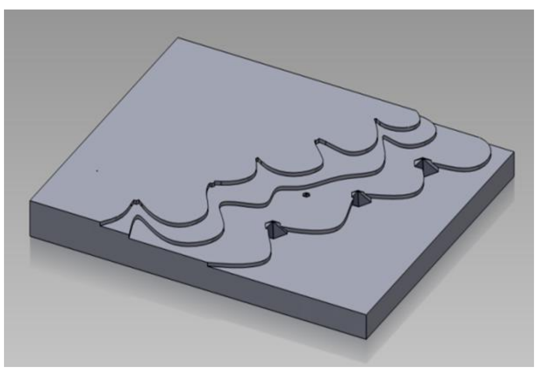
If the supersaturation is increased, at a bigger temperature gradient (≥5 K/cm), the mixed growth mode appears. The convection in liquid gallium solution starts. For some convection flow the macrosteps coexist with hillocks on the growing crystal surface.
The average growth rate achieves 2 µm/h.

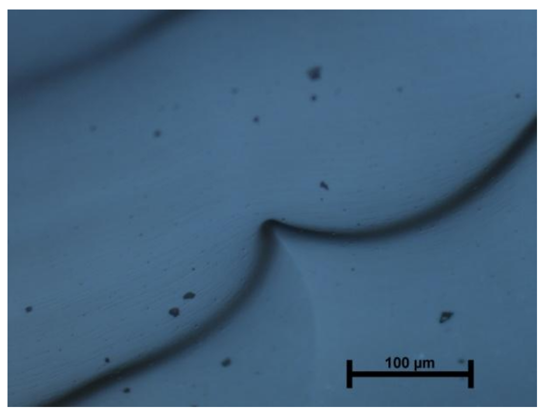


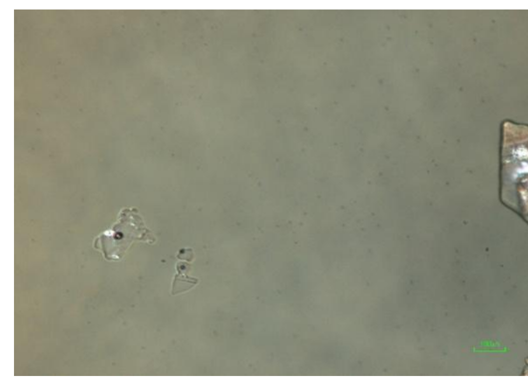


Seeded Growth
LPE Growth – The Multi Feed Seed Configuration

For higher supersaturation, at a bigger temperature gradient, the convectional velocity increases, the hillocks disappear and only the macrosteps are detected, beginning to play a dominant role on the growing crystal's surface. The growth rate attains even 5 µm/h. The stronger convective flow disturbs the macrosteps' propagation. This leads to the step bunching effect and macroscopically unstable growth with formation of voids and gallium inclusion in the HNPS-MFS-GaN.

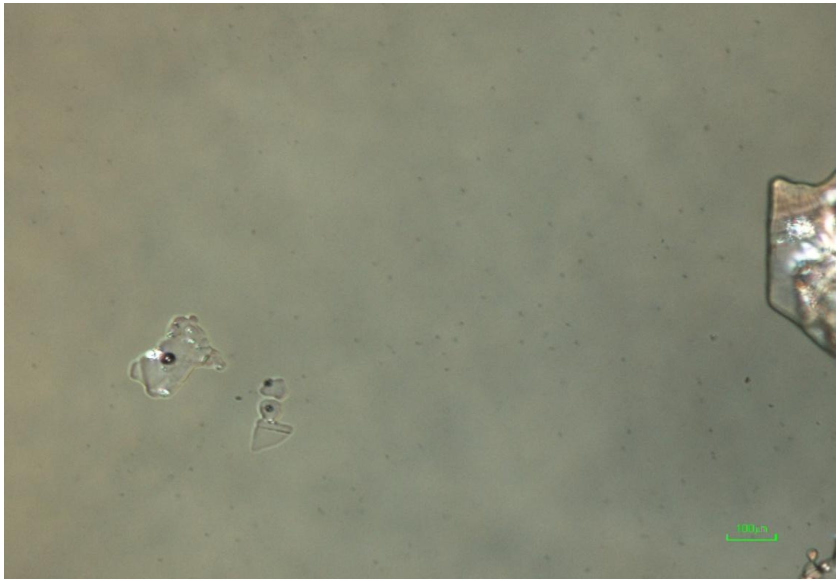






Seeded Growth
LPE Growth – The Multi Feed Seed Configuration

Macrosteps



Voids and gallium inclusions

Hillocks and mixed growth mode

No voids, no gallium inclusions

Hillocks or mixed growth modes are preferred!

Seeded Growth
LPE Growth – The Multi Feed Seed Configuration

The deposition of HNPS-GaN layers and dissolution of HVPE-GaN can improve the structural quality of the obtained crystals. The XRCs are narrower and the lattice bowing radii increase. For the (002) reflection the FWHM of the HNPS-MFS-GaN can be equal to 100 arcsec.

The absolute value of the bowing radius can be increased from 2 m to 20 m.

The formation of the HNPS-GaN layer on the HVPE-GaN substrate significantly changes the bowing radius of the crystal if only the HVPE-GaN and the HNPS-MFS-GaN are elastically strained.

Almost total dissolution of the HVPE-GaN substrate helps to release the stress in the HNPS-MFS-GaN .

The bowing radius of the HNPS-GaN crystal increases in comparison to the seed.

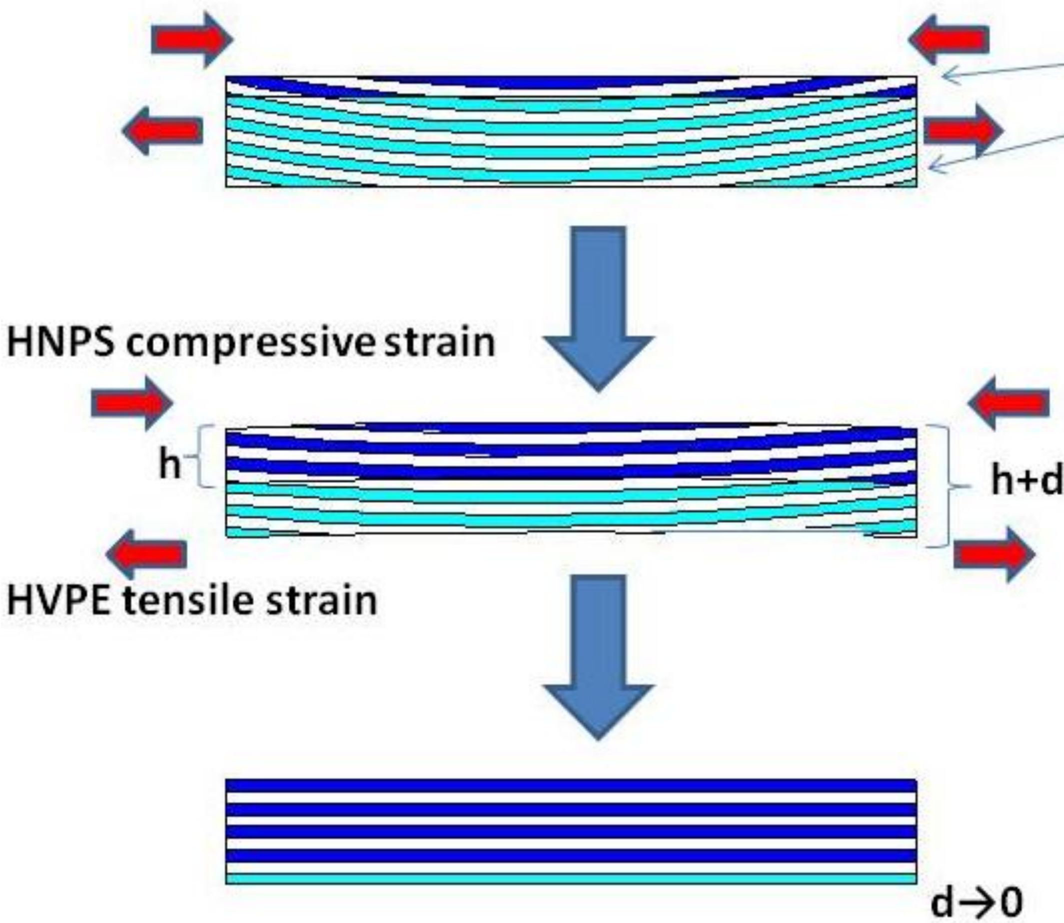
Due to the difference in the *a* lattice constant between the HVPE-GaN and the HNPS-MFS-GaN, the pressure grown material is under compressive strain and the HVPE-GaN seed is under tensile strain during the crystallization process.

The HVPE-GaN dissolves from its (000-1) surface.

The HNPS-MFS-GaN becomes thicker and thicker.

The compressive strain for the HNPS-MFS-GaN has to be decreased in time and finally the pressure grown crystal can be structurally flatter.

Seeded Growth
LPE Growth – The Multi Feed Seed Configuration



$a_{HNPS\text{-}MFS\text{-}GaN} = 3.1893$ Å
$a_{HVPE} = 3.1885$ Å

$\Delta\varepsilon = (a_{HNPS\text{-}MFS\text{-}GaN} - a_{HVPE})/a_{HVPE}$

$\kappa = 6\,\Delta\varepsilon\, h\, d/(h+d)^3$

$R = 1/\kappa$

$\Delta\varepsilon$ - strain
κ - curvature
h - thickness of the HNPS-MFS-GaN
d - thickness of the HVPE-GaN
R - bowing radius

Seeded Growth
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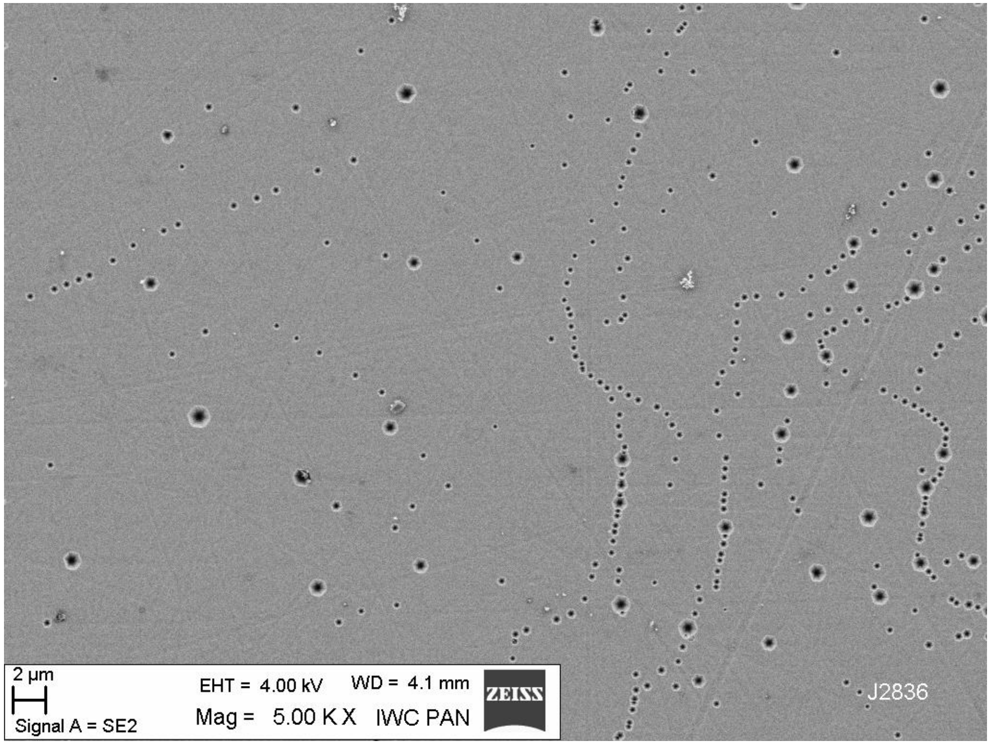
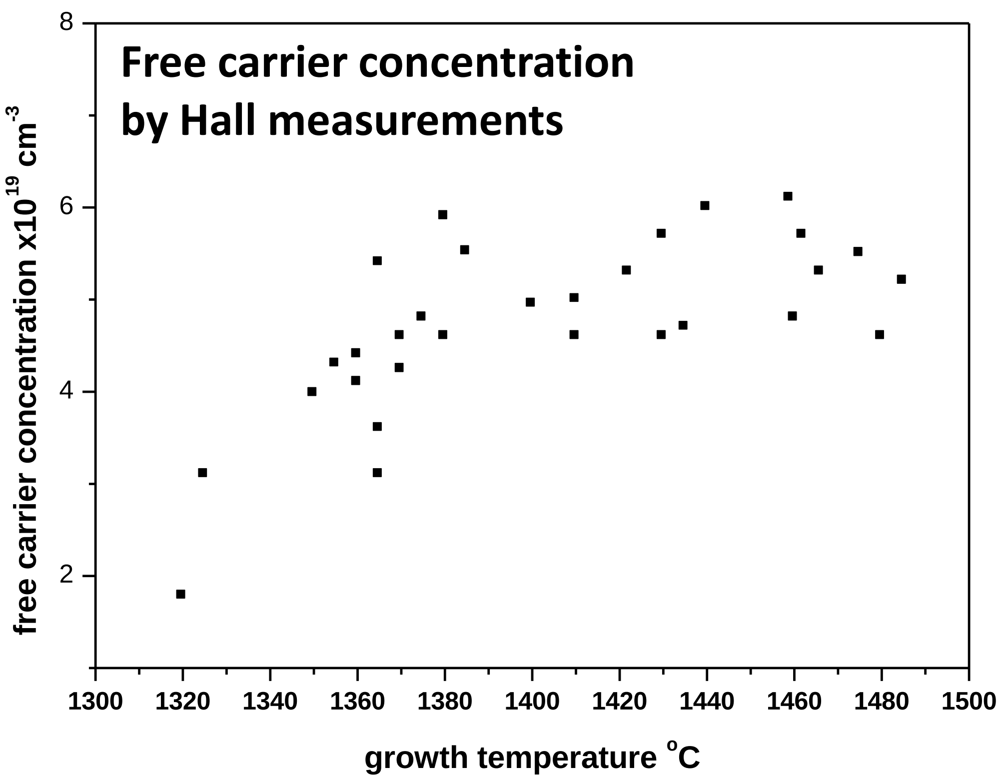
The average etch pit density for the HNPS-MFS-GaN is of the order of $1x10^6$ cm^{-2}.
The growth of several hundred microns of the HNPS-MFS-GaN allows to reduce the threading dislocation density by a factor of 5.



Etching performed in the liquid eutectic of KOH and NaOH at temperatures ranging from 673 to 723 K.

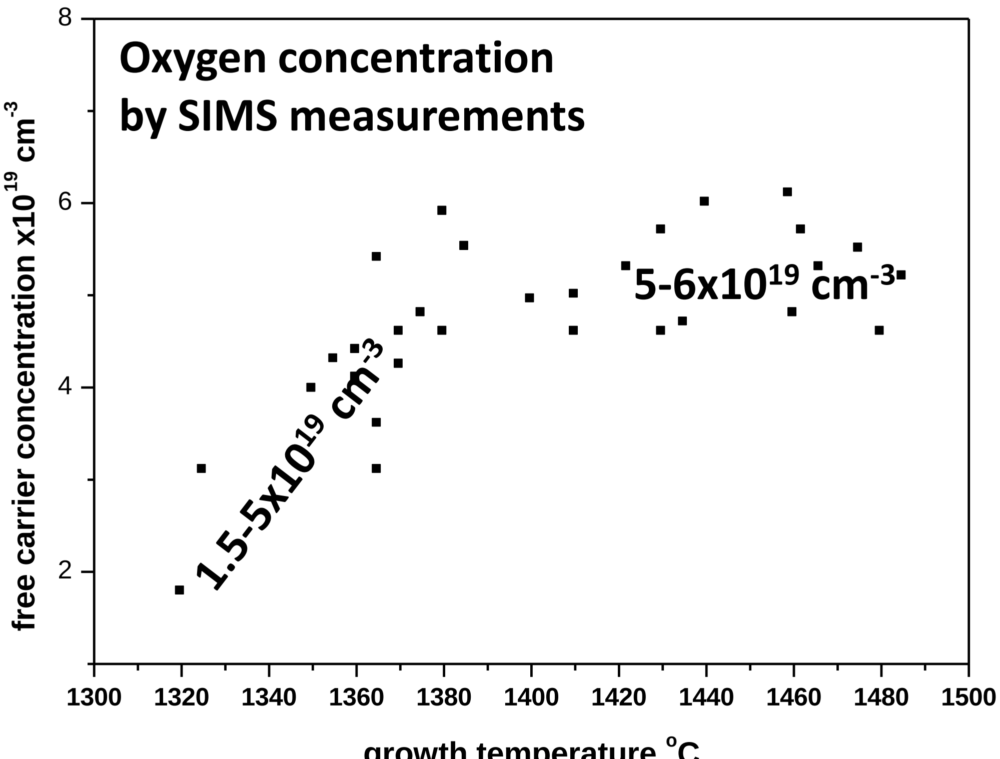
Seeded Growth
LPE Growth – The Multi Feed Seed Configuration

The free carrier concentration for the HNPS-MFS-GaN crystals is always higher than 10^{19}cm^{-3} and its value depends on the growth temperature.
With an increase of the growth temperature from 1593 to 1723 K, the carrier concentration in the HNPS-MFS-GaN increases. For higher temperatures (higher than 1723 K), it is saturated and reaches a constant value of the order of 5 x 10^{19} cm^{-3}.



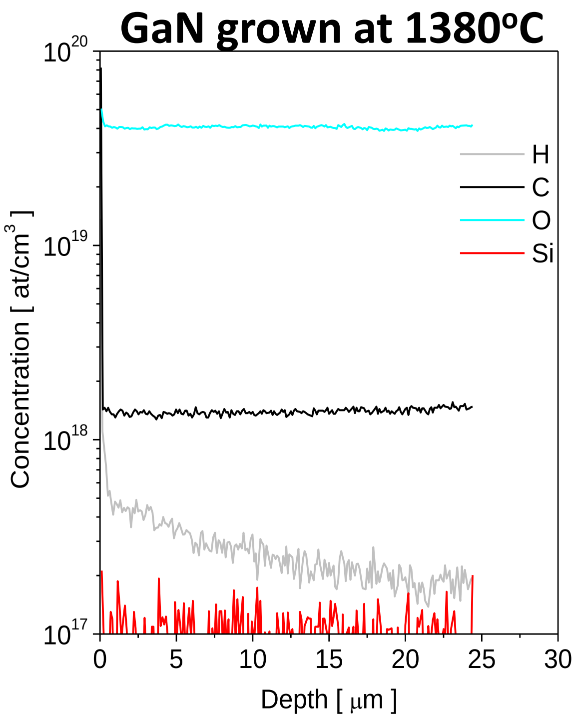
Seeded Growth
LPE Growth – The Multi Feed Seed Configuration

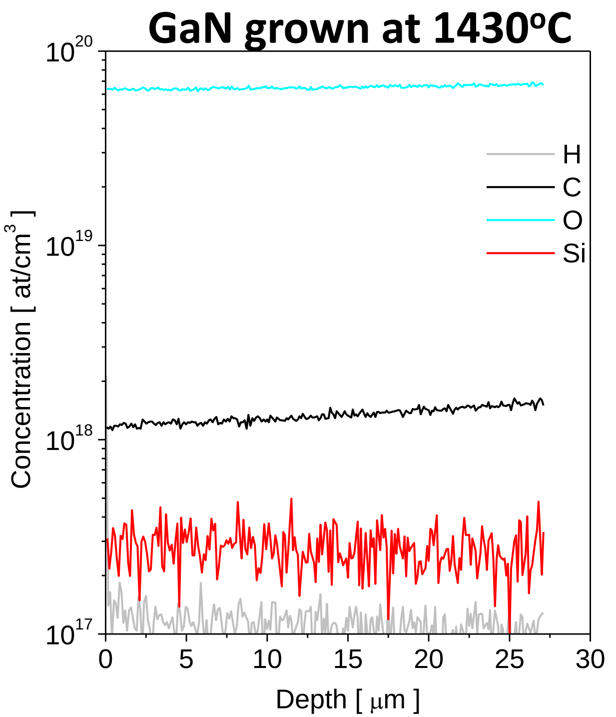
This high free electron concentration in HNPS-MFS-GaN is associated with high oxygen concentration in the material. The level of the oxygen impurity in the crystals is just the same as the level of the free carrier concentration. Lower oxygen concentration is noted for a lower growth temperature.



Seeded Growth
LPE Growth – The Multi Feed Seed Configuration

The oxygen atoms in the HNPS-MFS-GaN crystals originate from liquid gallium. The increase of the oxygen content in the GaN crystals together with the increase of the growth temperature results from higher solubility of oxygen in liquid gallium at high temperature and high pressure. When the temperature reaches a certain value, the solubility limit of oxygen in liquid gallium can be observed. Thus, even for higher temperatures, the oxygen and free carrier concentrations do not increase.



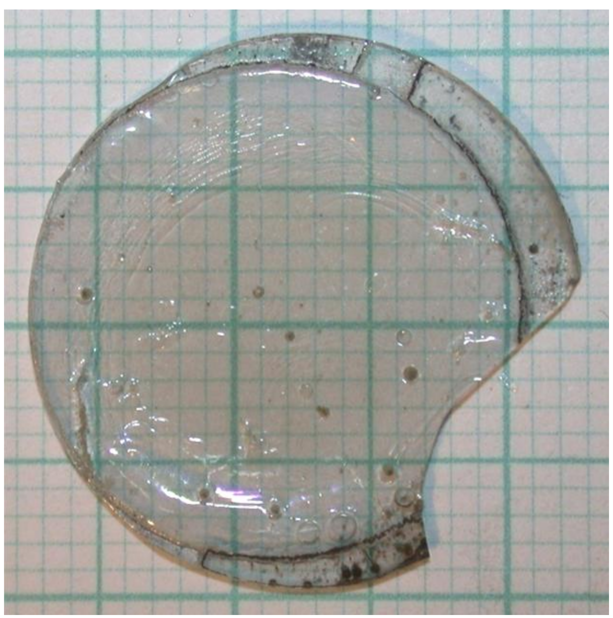


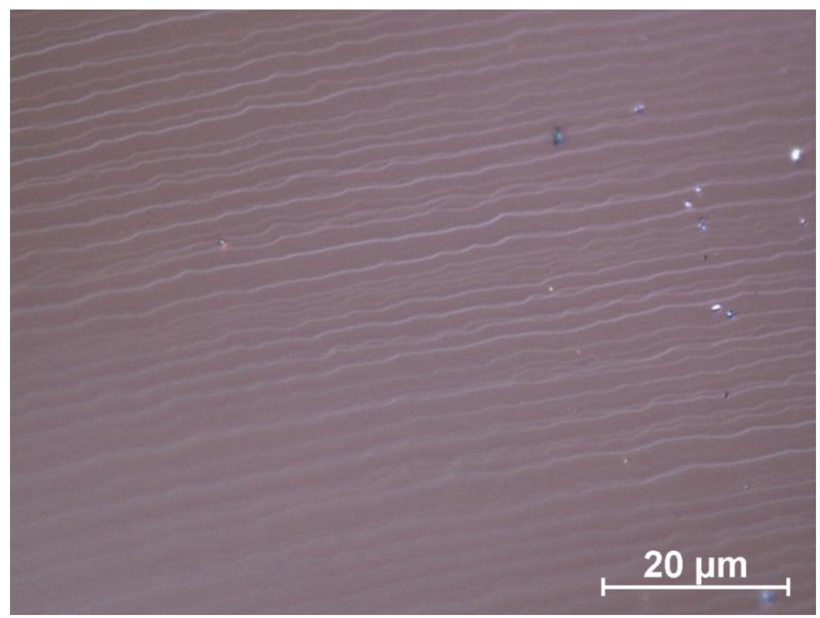
Seeded Growth
LPE Growth – The Multi Feed Seed Configuration

For the HNPS-MFS-GaN crystallization in the solution of Ga:Mg (up to 1 at% of Mg in the solution) the typical morphology observed is the macrosteps propagation. The growth rate varies from 1 to 2 μm/h. Gallium inclusions or voids in the material are not observed.

The addition of Mg to the Ga solution would drastically change some properties of the solution, mainly its viscosity.

Some changes in the composition of the solution can prevent the formation of the voids and inclusions while maintaining a relatively high growth rate.

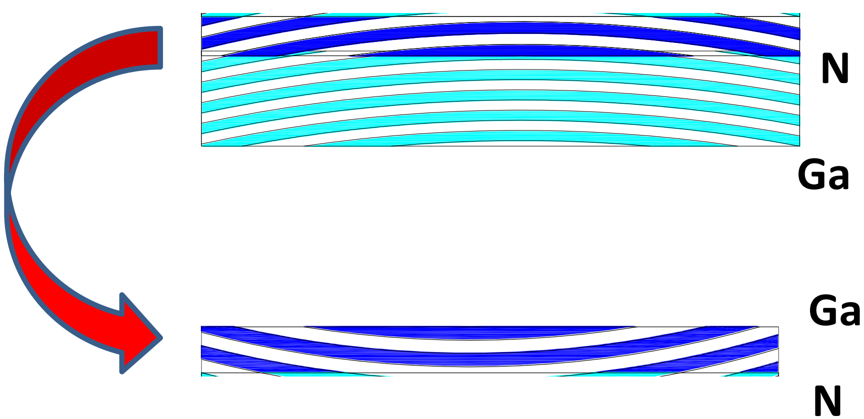


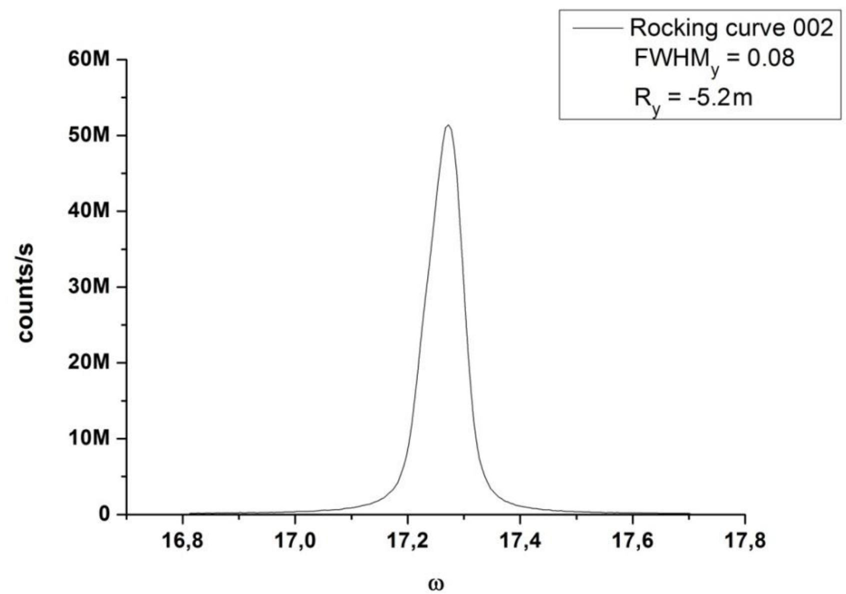


Seeded Growth
LPE Growth – The Multi Feed Seed Configuration

The XRC FWHM and the bowing radii of the HNPS-MFS-GaN:Mg crystals are not changed significantly, comparing to the HVPE-GaN seeds.
The *a* lattice constant of the HNPS-MFS-GaN:Mg is the same as for the F-S HVPE-GaN seed. There is no difference in strains for these two layers. The F-S HVPE-GaN seed is structurally reproduced by the high pressure material.
Since the (0001) surface of the examined material is situated close to the HVPE-GaN seed, the average etch pit density for the HNPS-MFS-GaN:Mg is always of the order of 5 x 10^6 – 10^7 cm^{-2} (as for the HVPE-GaN seed).

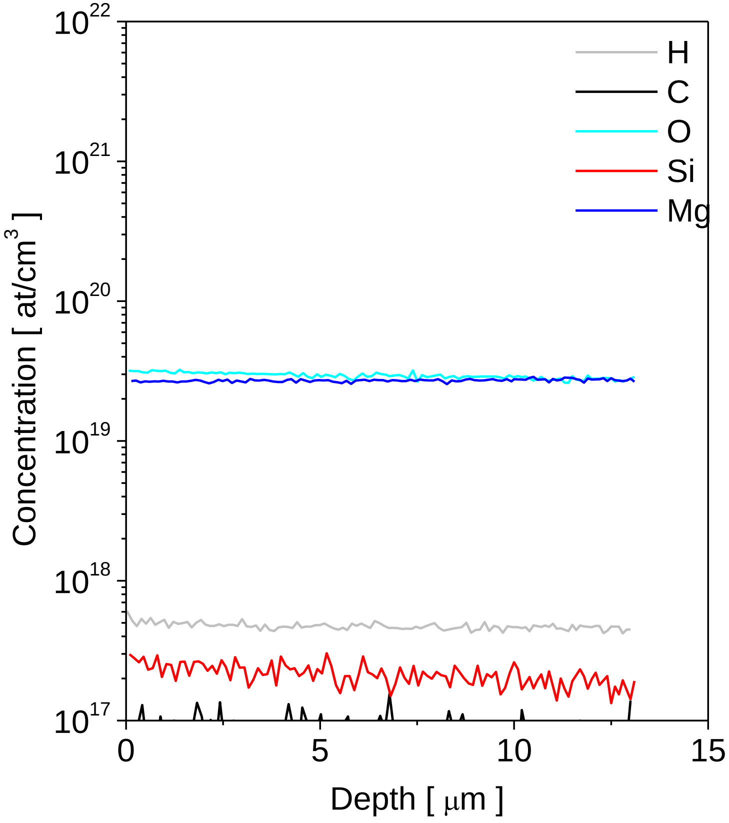
a_{HNPS} - 3.1885 Å
a_{HVPE} - 3.1885 Å





Seeded Growth
LPE Growth – The Multi Feed Seed Configuration

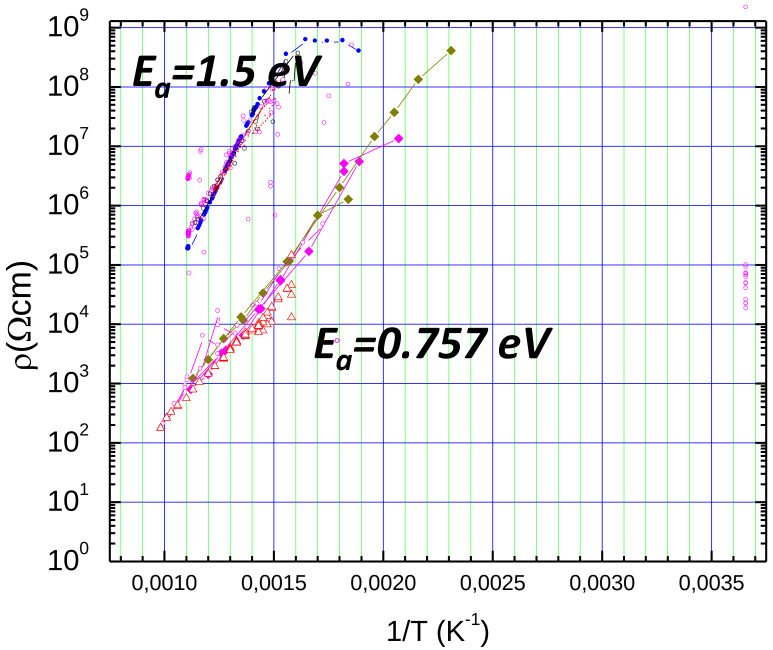
Magnesium concentration in the HNPS-MFS-GaN:Mg crystals is strictly the same as oxygen concentration.
The magnesium impurity compensates the oxygen donor in the pressure grown material.



Seeded Growth
LPE Growth – The Multi Feed Seed Configuration

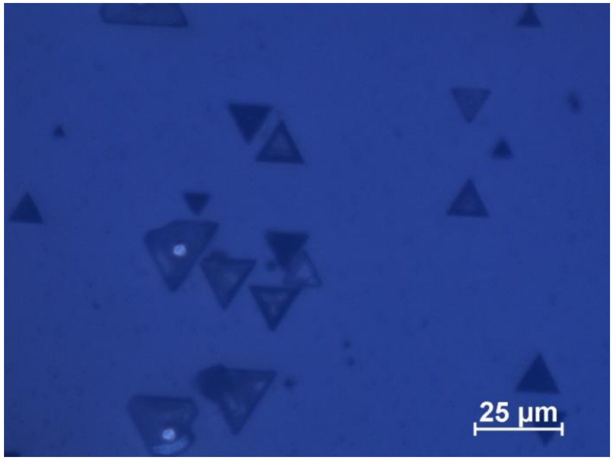
The crystals are semi-insulating at room, as well as higher (1073 - 1173 K) temperatures and their electrical properties are very stable. Resistivity at room temperature was estimated at 10^{15} - 10^{16} Ω·cm for crystals grown at higher temperatures (1693-1723 K) and 10^{11} - 10^{12} Ω·cm for crystals grown at lower temperatures (1653-1693 K).

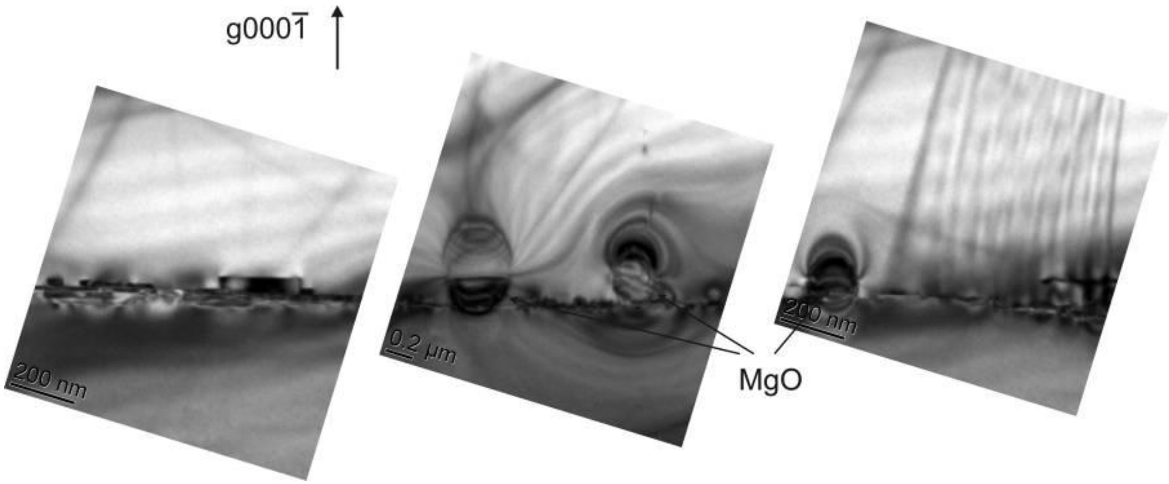
For the same magnesium concentration in the solution (and presumably in the crystals) the resistivity depends on the growth temperature and is lower for crystals grown at low temperatures. This seems to be associated with the oxygen concentration in the solution and in the crystals.



Seeded Growth
LPE Growth – The Multi Feed Seed Configuration

The biggest disadvantage of the HNPS-MFS-GaN:Mg crystals are the precipitates of small magnesium oxide crystallites. They are mainly formed at the interface between F-S HVPE-GaN seed and the new pressure grown material. Some precipitates also exist in the volume of the HNPS-MFS-GaN:Mg crystal.
The affinity of oxygen with magnesium is so high that during crystallization process, especially at the beginning of the growth, the formation of the MgO crystals takes place.





Seeded Growth
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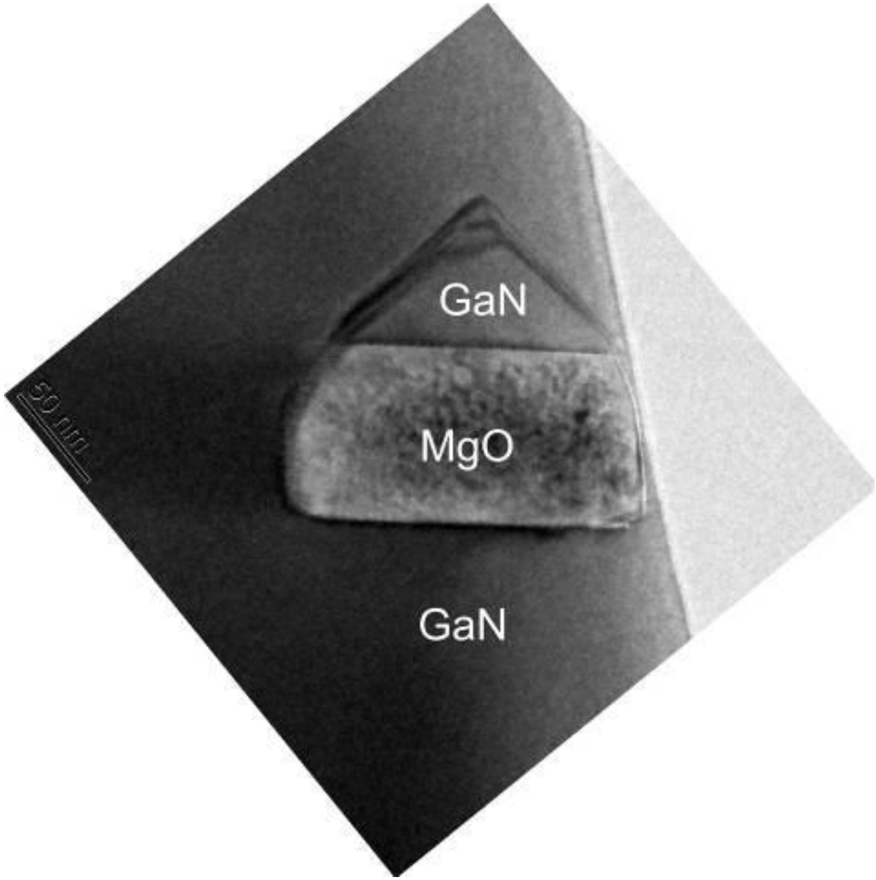
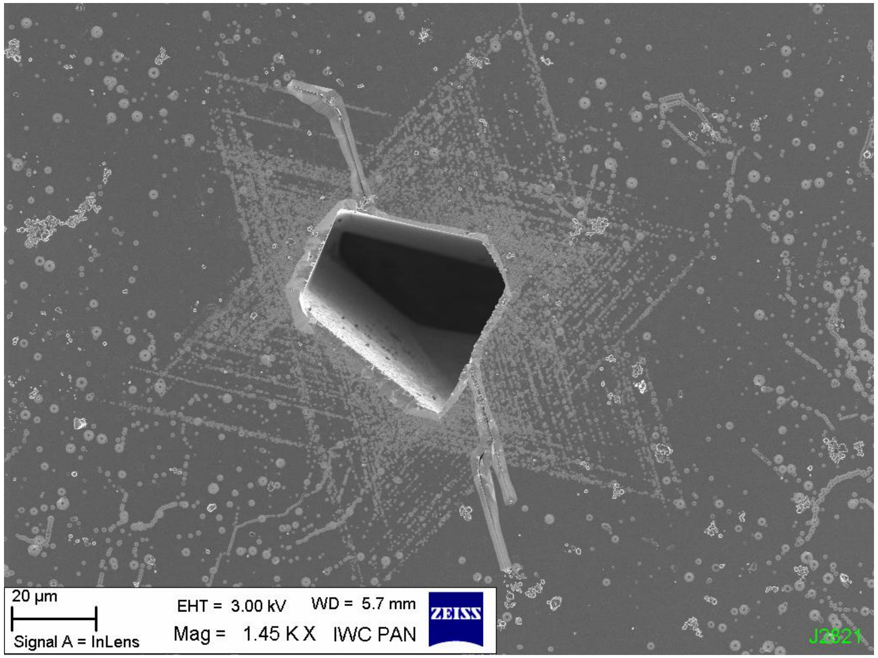
The MgO crystals are overgrown by the HNPS-MFS-GaN:Mg.
During the preparation of HNPS-MFS-GaN:Mg substrates the MgO crystals or voids after them can create some big pits in the nitride material.





Seeded Growth
LPE Growth – The Multi Feed Seed Configuration

One way to improve the structural quality of the HNPS-MFS-GaN is to use high quality HVPE-GaN crystals as seeds. It has been shown that using ammonothermally grown GaN (as a seed) one can obtain high quality FS HVPE-GaN.