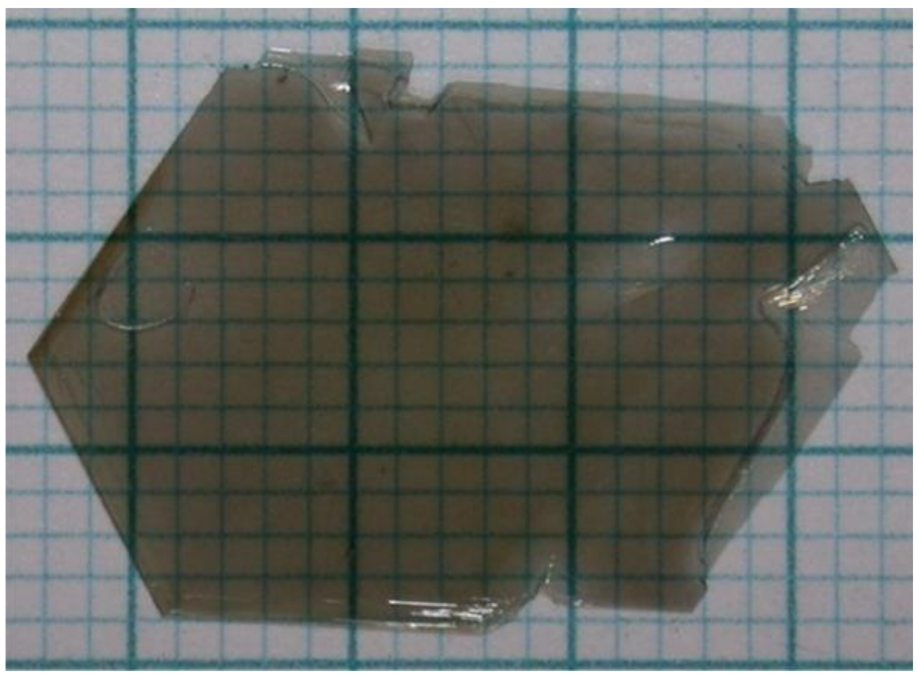
High Nitrogen Pressure Solution (HNPS) growth method

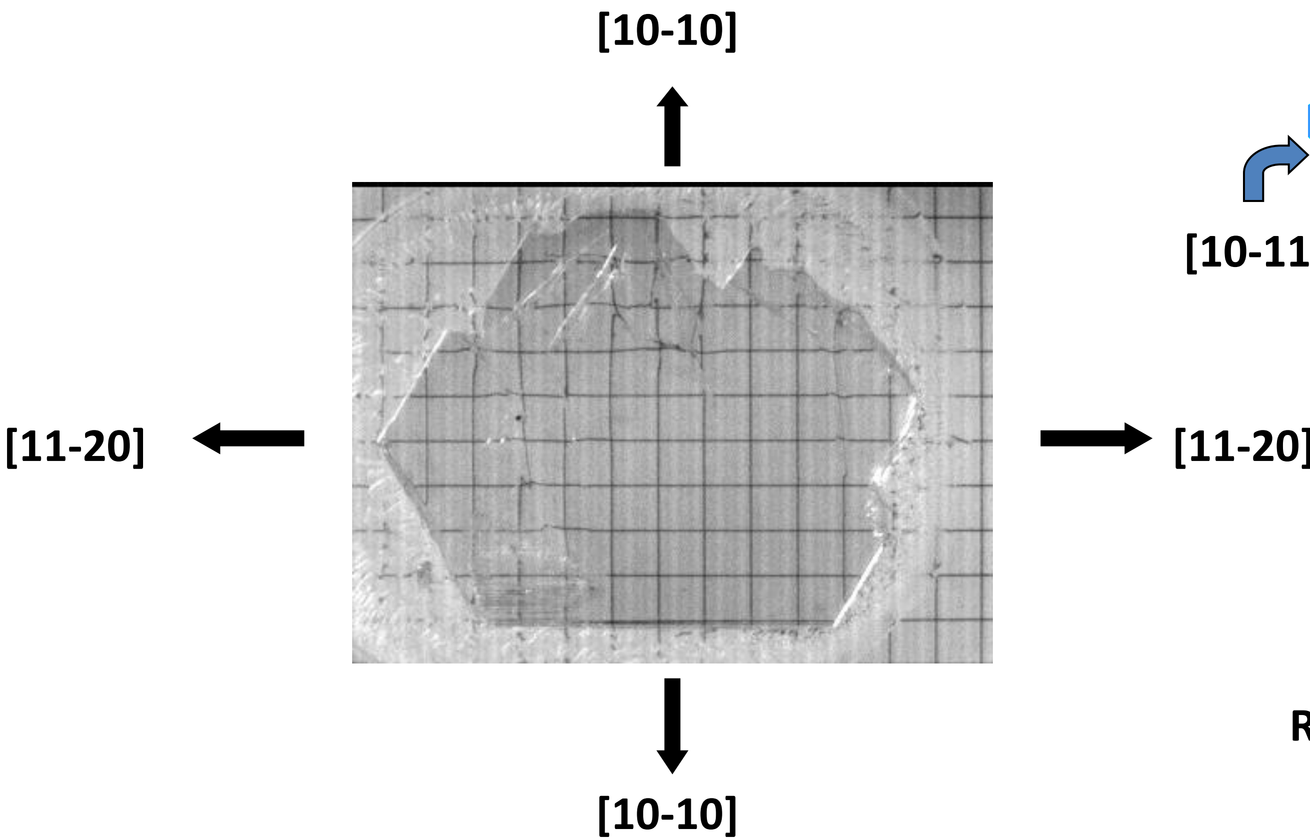
Spontaneous Crystallization

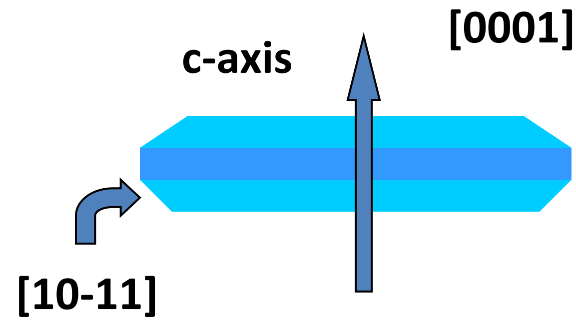
The crystallization without seeds in the solution is called spontaneous crystallization.
The dominating morphological form of GaN crystals grown by this method is a hexagonal platelet.
The maximum lateral size of the platelet is 3 cm^2, whereas the thickness about 150 µm.



Spontaneous Crystallization

The crystals in the form of hexagonal platelets grow slowly, at a rate lower than 0.1 mm/h, into [10-10] directions (perpendicular to the c-axis).





$R_{11\text{-}20} > R_{10\text{-}10} >> R_{0001}$

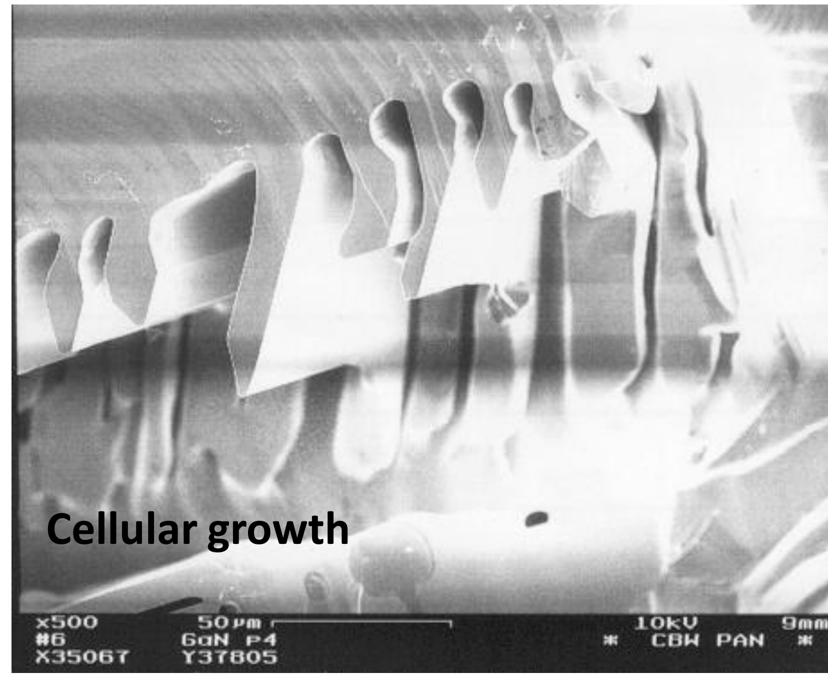
$R_{0001} \cong 1\ \mu m/h$

Spontaneous Crystallization

The single crystals are slightly gray or transparent, very often with flat mirror-like faces. The tendency for unstable growth is stronger for the polar (0001) faces of the platelets. The opposite surface is mirror-like and often atomically flat.

N-face is always flat: very fast lateral growth at very slow nucleation

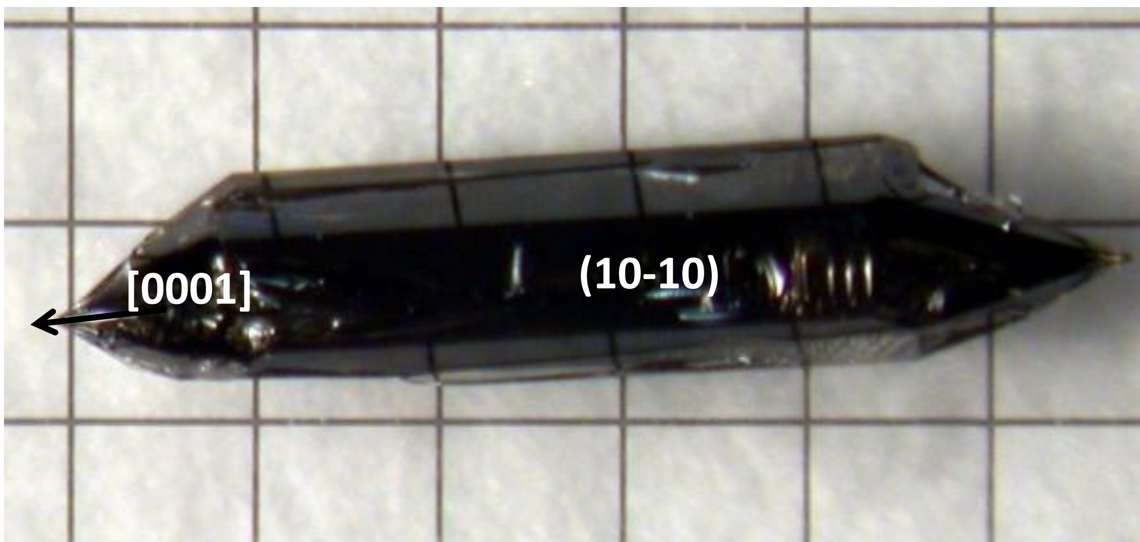
Ga-face is often non flat: instability

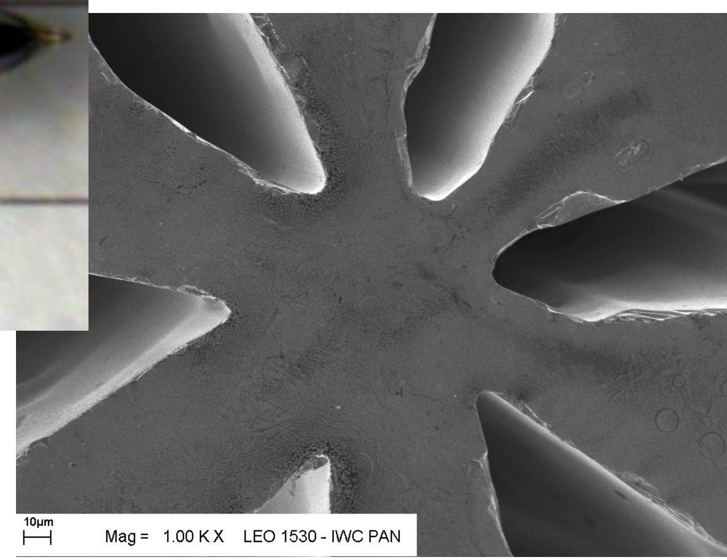


The morphological features like macrosteps, periodic inclusions of solvent or cellular growth structures are observed on this side. For crystals grown without intentional doping the unstable surface always corresponds to the Ga-polar (0001) surface of GaN.

Spontaneous Crystallization

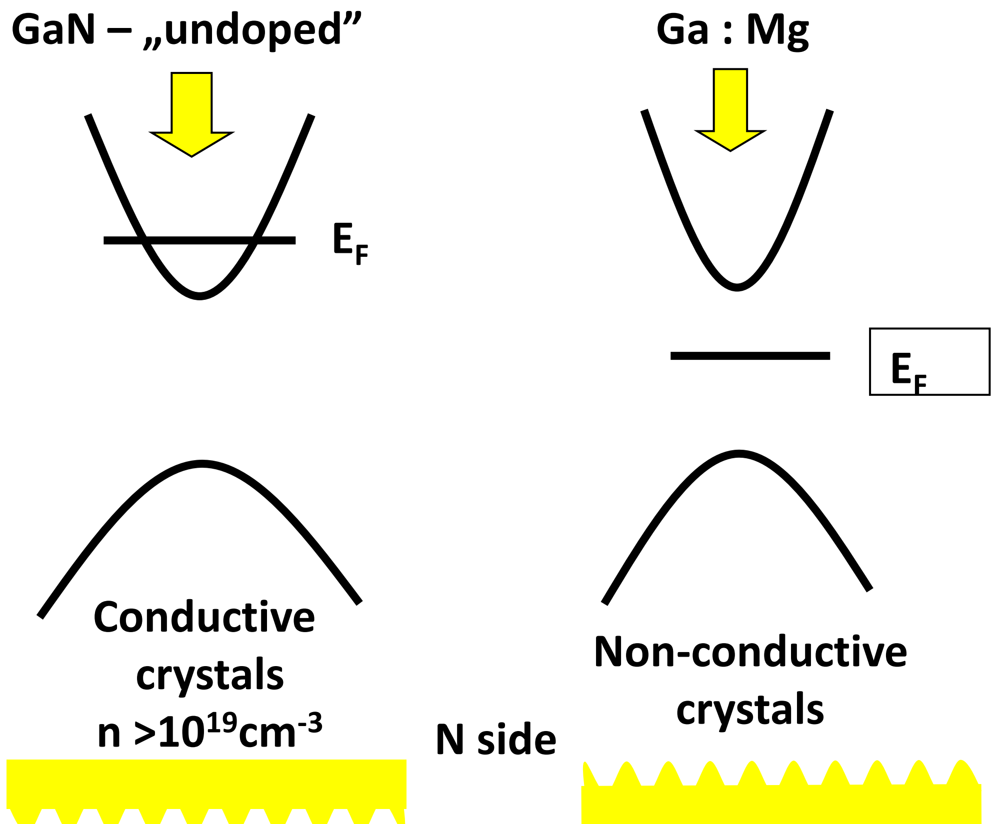
The second possible form of the pressure grown crystals is a needle. The needles are elongated into c-direction, with a diameter of about 1 mm and up to 10 mm in length.
The GaN needles are strongly unstable crystals. They are dark due to the presence of microdefects such as dislocation loops and gallium inclusions that are the result of a fast and unstable growth in the c-direction. These crystals are often hollow from inside.

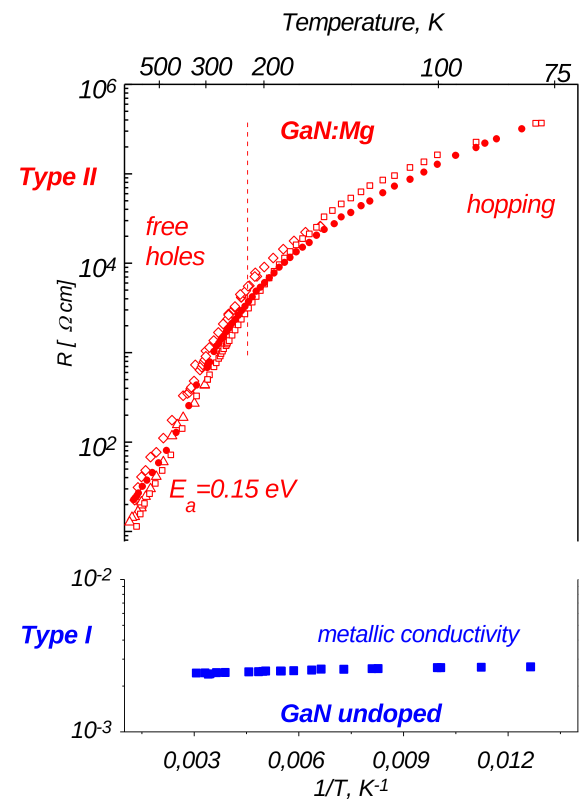




Spontaneous Crystallization

The HNPS-GaN crystals are strongly n-type, with uniform free electron concentration of about 5 x 10^{19} cm^{-3} and carrier mobility of about 60 cm^2 V^{-1} s^{-1}.
The high free carrier concentration occurs due to the presence of oxygen. The level of the oxygen impurity in the GaN crystals is exactly the same as the level of the free carrier concentration.
These free carriers can be fully eliminated by the Mg acceptor added into the solution.

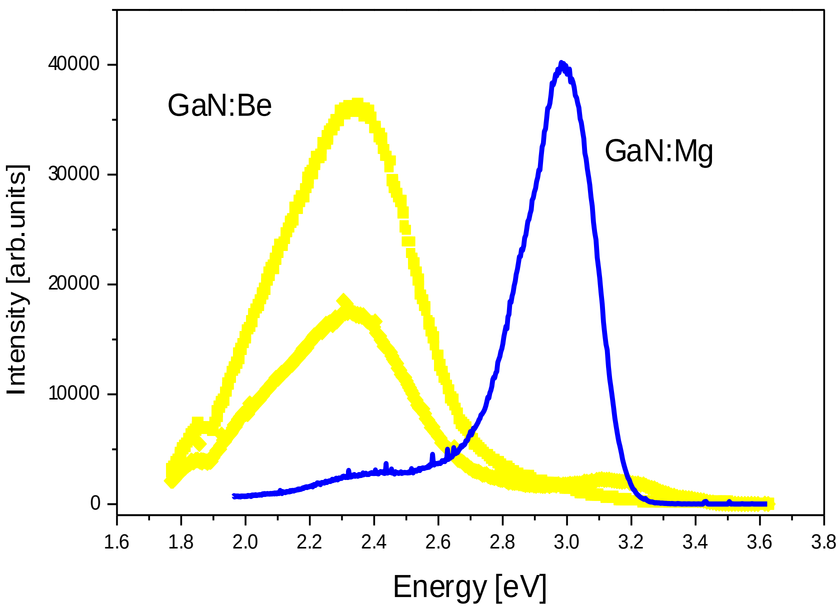




E. Litwin-Staszewska et al., J. Appl. Phys. 89 (2001) 7960.

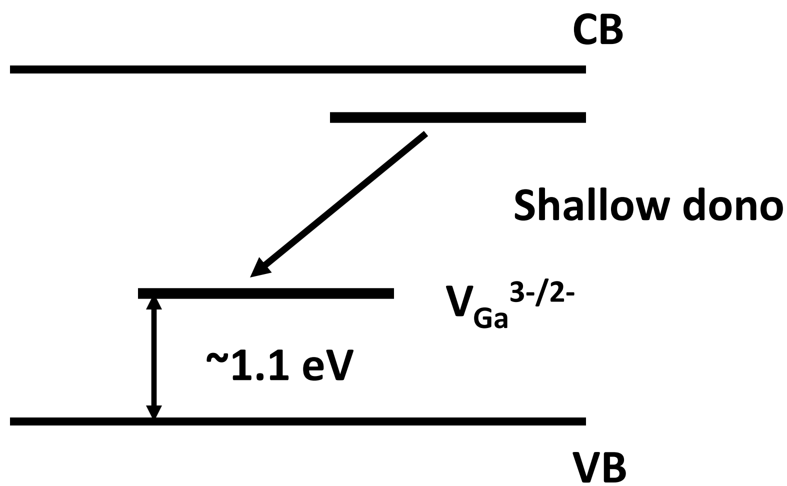
Spontaneous Crystallization

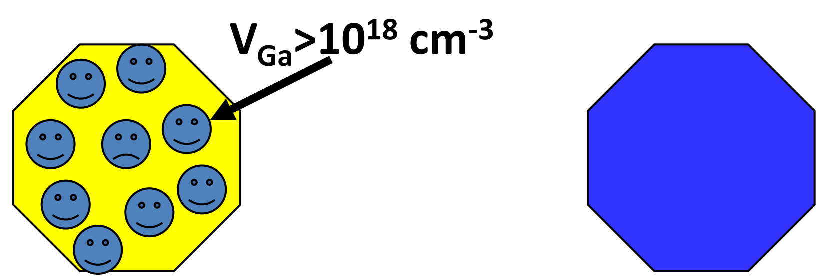
High concentration of gallium vacancies was found in the conductive crystals in contrast to the Mg-doped samples where the vacancies were not observed.
The presence of the native point defects in the crystals was checked by positron annihilation measurements.
The difference in the PL spectra of the conductive (strong yellow emission) and Mg-doped crystals (no yellow emission, but blue Mg-related signal) revealed that the gallium vacancies are involved in the strong yellow luminescence in GaN.



P. Perlin, J. Appl. Phys. Lett. 67 (1995) 2524.

K. Saarinen et al., Phys. Rev. Lett. 79 (1997) 3030.

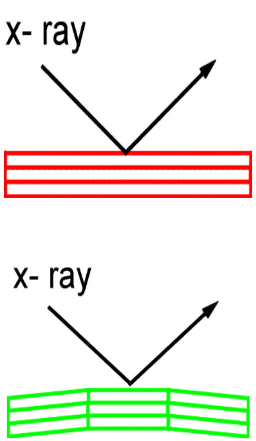


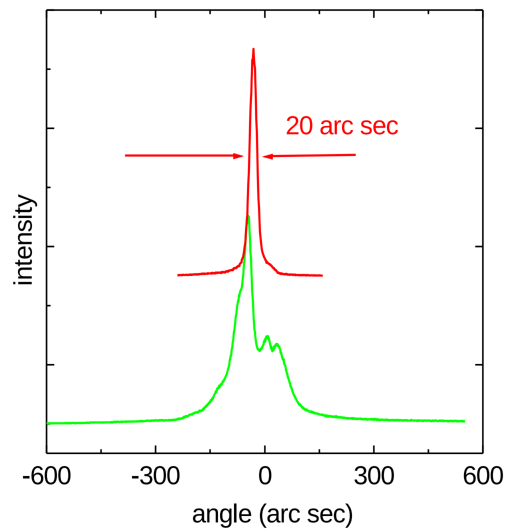


Spontaneous Crystallization

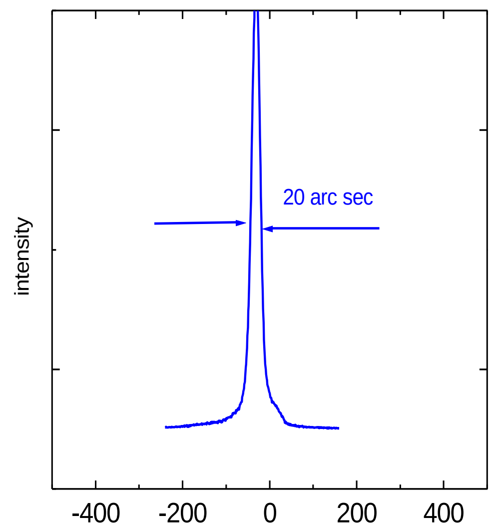
The structure of the spontaneously pressure grown GaN crystals was studied by XRD. The crystallinity depends on the size of the crystal. The full width at half maximum (FWHM) for the (002) reflection is of the order of 50 arcsec for a 1–3 mm large crystals. For larger platelets the x-ray rocking curve (XRC) often splits into a few peaks, showing the presence of low angle boundaries separating grains of a few millimeters in size.

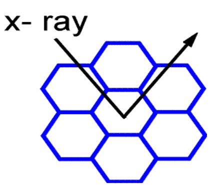
symmetrical reflection 00.2





in plane reflection 22.0





Typical for Mg-doped GaN and best undoped GaN

Tilt mosaicity observed for some undoped GaN

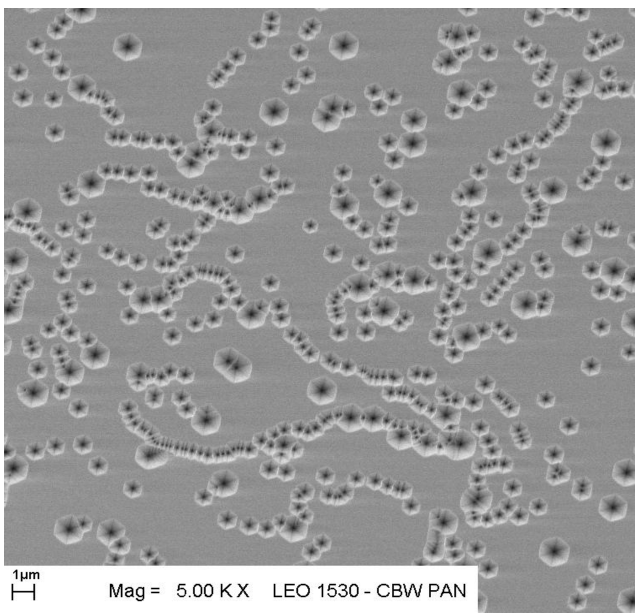
No twist mosaicity

M. Leszczynski et al., J. Cryst. Growth 169 (1996) 235

Spontaneous Crystallization

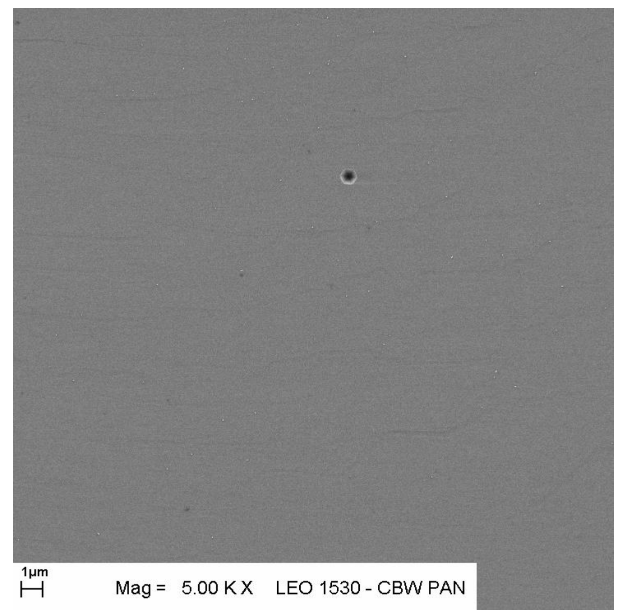
In order to determine the dislocation density in GaN crystals, the defect selective etching (DSE) method has been developed. It was proved that etching in molten KOH–NaOH eutectic (at 723 K) reveals dislocations in GaN pressure-grown single crystals. The etch pit density in HNPS-GaN, estimated by counting the etch pits in a given area, is very low, of the order of 10^2 cm^{-2}.

MOCVD GaN on Al_2O_3



10^8 – 10^9 cm^{-2}

Pressure grown GaN



10 – 100 cm^{-2}

L.J. Weyher, et al., J. Cryst. Growth 210 (2000) 151.

Spontaneous Crystallization

The main disadvantages of spontaneous crystallization by the HNPS method are: small size of crystals, poor reproducibility of the size, and the distribution of GaN crystals in the crucible