50 years of the Institute of High Pressure Physics Polish Academy of Sciences

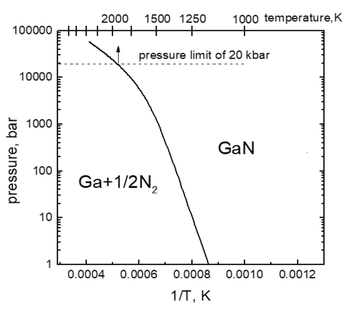
Highlights in III-V semiconductors, THz physics and nanomaterials

Anniversary Symposium „Unipress 50”

From spontaneous nucleation to controlled growth - the past and present of GaN crystallization at IHPP PAS

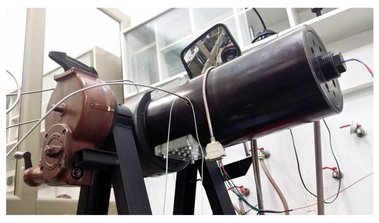
NL3 — Crystal Growth Laboratory

HNPS method



Phase diagram of GaN.

Since the high temperature solution growth of GaN requires high nitrogen pressure, gallium nitride has always been in the field of interest of the Institute of High Pressure Physics of the Polish Academy of Sciences (formerly High Pressure Research Center PAS). In 1984 Karpinski et al. [1] determined the equilibrium nitrogen pressure–temperature curve for gallium nitride in the temperature range up to 2000 K. At the beginning of the 1990s, on the wave of nitrides popularity, the thermodynamic background of the system Ga–GaN–N_2 and thermodynamic properties of GaN were determined and formulated [5]. By the end of 1995 small GaN platelets (up to 2 mm) were obtained. In 1996, 1 cm^2 and 100-µm -thick GaN crystal (platelet) of perfect structural quality and low dislocation density (10^2 cm^{-2}) was obtained for the first time. Based on this success, relatively fast development of the Crystal Growth Laboratory was observed. The quantity of high pressure (HP) reactors (Institute’s home-made apparatus) increased several times during a few years. The interior diameter, and thus the working volume of the HP chamber also increased. The development of high-pressure crystallization allowed for an analysis of the growth morphology, large-scale studies of the properties of the obtained crystals, and set prospects for further research on optimizing GaN crystallization.



HP reactor for GaN crystalization.

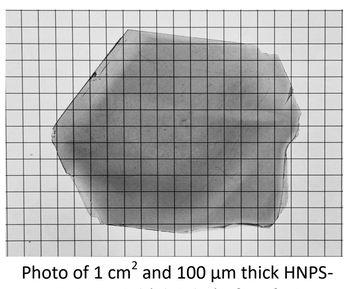
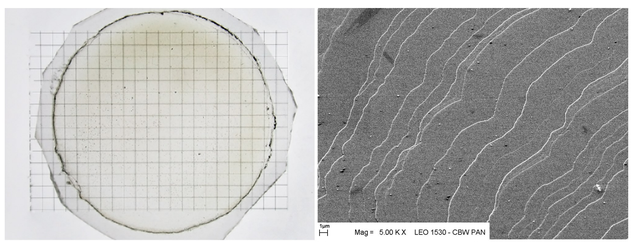
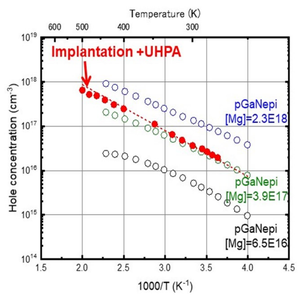


Photo of 1 cm^2 and 100 µm thick HNPS-GaN crystal (platelet) of perfect structural quality and low dislocation density (10^2 cm^{-2}) derived from spontaneous nucleation.



From left: crystal obtained by Multi-Feed-Seed (MFC) process, growth morphology in HP reactors. [3]

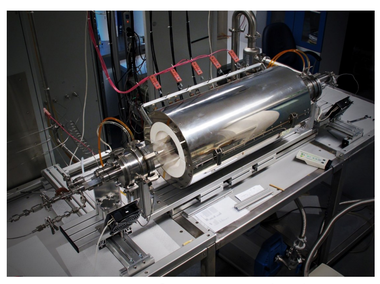
Currently, crystallization of GaN in HP autoclaves is not continued. The chambers are used to conduct UHPA (Ultra High Pressure Annealing) processes of implanted crystals with ions of various elements.



The result of UHPA of Mg-implanted GaN substrate.

Mg_{Ga}- acceptor activation ratio (N_A/[Mg]) ≥78 %

HVPE method



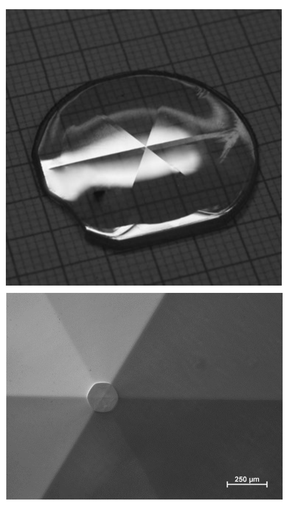
HVPE reactor for GaN crystalization.

In parallel with the development of the high-pressure GaN growth method, IHPP PAS decided to also develop the Halide Vapor Phase epitaxy (HVPE) growth method. In 2004, the first HVPE reactor was built. The development of the second growth method allowed for the establishment of growth technology on GaN/Al_2O_3 substrates and obtaining of the Institute's first 2-inch diameter separated GaN crystal [5].

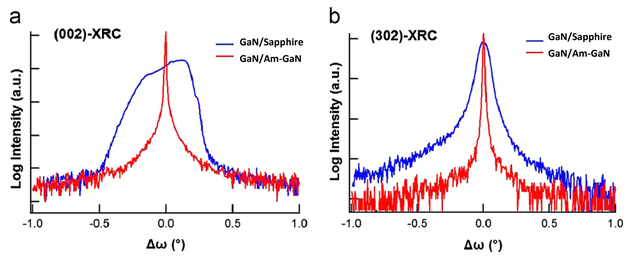
From the left a) GaN grown on MOVPE GaN/sapphire/Ti mask, b) self lift-off, c) 2-inch 1-mm-thick free-standing HVPE-GaN.

A high growth rate and high purity of crystals are the most important advantages of growth from the gas phase. Heteroepiaxial growth allowed obtaining GaN with threading dislocation density of 10^6 cm^{-2} and with crystallographic planes radii up to 10 m for 2-inch crystals. However, improving structural quality through heteroepitaxial growth seemed to be futile. The start of cooperation with Ammono Ltd. helped to change the status quo. Homoepitaxial growth on high-quality seeds was the best solution for further development of GaN crystallization by the HVPE method.

The first crystal with a high structural quality and high purity was obtained in 2013. [6] Limiting factors for the growth of bulk GaN such as growth anisotropy were identified.



Over 1-mm-thick as-grown HVPE-GaN crystal. Morphology of the grown crystal realized on a single hillock.



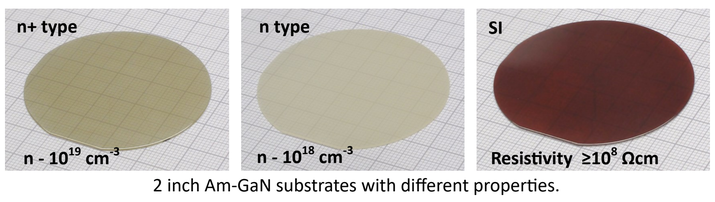
X-Ray rocking curves measured for GaN grown on foreign (blue) and native (red) substrate for reflections: a) (002) b) (302).

These factors are common for all crystallization methods of this important semiconductor. The development of the HVPE method proceeded in the direction of intentional doping with electron-donor and electron-acceptor elements. [7] Methods of doping with silicon or germanium to obtain conductive crystals were determined. Similarly, the way to dope with manganese, iron, or carbon to grow semi-insulating material was developed. Further research is aimed at obtaining GaN with exceptional purity and reducing lateral growth in bulk crystallization.

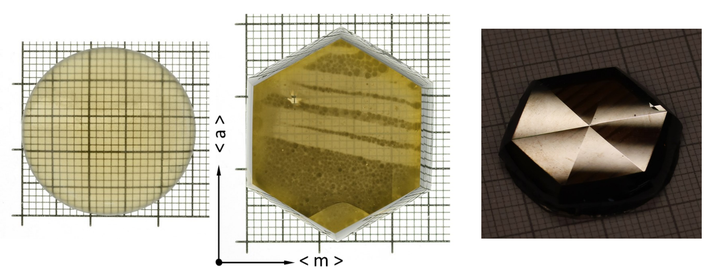
Ammonothermal method

Hall of ammonothermal autoclaves.

First the cooperation, then the lease, and the eventual purchase of Ammono by tender was the course of the relationship with IHPP PAS. The machinery, reactors and technology were incorporated into the NL-3 Crystal Growth Laboratory. The pilot line produces two-inch GaN conductive substrates with different carrier concentrations (n-type) and highly resistive substrates (semi-insulating) with the highest structural quality in the world. Supported by the R&D department, it implements processes in which growth is carried out in special matrices that force crystallization in one direction. [8] Intensive research is currently underway to: understand the nature of growth in supercritical ammonia, standardize the surface preparation and shape of the seeds, and its effect on the course of crystallization and the quality of the obtained crystals. [9]

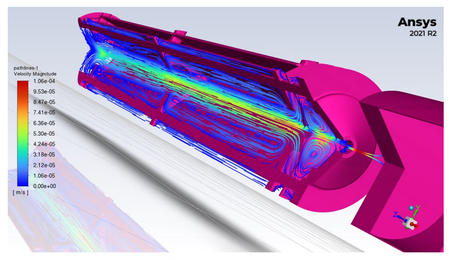


2 inch Am-GaN substrates with different properties.

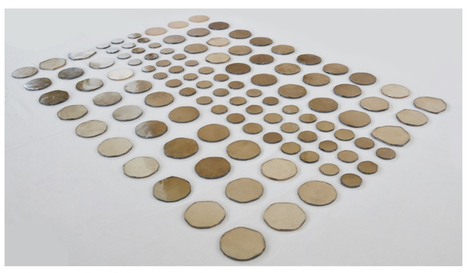


From the left: round seed with lenticular shape (lens seed), hexagonal crystal grown on lens seed, growth morphology on lens shape seed.

Solutions are being sought for obtaining crystals and substrates larger than 2 inches in size. In addition, simulations of temperature distribution and reactant distribution in autoclaves are being conducted.



Results of reagent flow calculations in the ammonothermal autoclave. Stream lines in the growth zone.



The result of the crystallization process in an ammonothermal autoclave. (Photo of 1-inch and 2-inch crystals)

The results of the study and the implementation of new solutions for optimizing the growth allowed to double the growth rate without deteriorating the structural quality of the obtained crystals. [10]

References

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[9] Sochacki T. et al. **Fundamental Studies on Crystallization and Reaching the Equilibrium Shape in Basic Ammonothermal Method: Growth on a Native Lenticular Seed.** Materials 2022, 15(13), 4621.
[10] Kucharski R. et al. **Growth of bulk GaN crystals**. J. Appl. Phys. 2020 128, 050902.

Summary

- High-pressure chambers are used to conduct UHPA (Ultra-High-Pressure Annealing) processes of implanted crystals with ions of various elements (p-type has been presented).
- Currently, GaN crystallization in the laboratory is realized by two methods: HVPE - from the gas phase, and ammonothermal - from ammonia solution.
- The synergy of the two technologies (ammonothermal and HVPE) made it possible to obtain a wide range of substrates with high structural quality and specified properties.
- The ammonothermal method guarantees the world's best structural quality and the possibility of mass production.
- The HVPE method makes it possible to multiply the quality of ammonothermal substrates and obtain GaN of high purity or intentionally doped with selected dopants.

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