Nitride semiconductors (GaN, AlN, InN) and their AlInGaN alloys are known for applications in power and high frequency electronics as well as optoelectronics (white LED light sources, blue, and green semiconductor lasers). Most devices are currently deposited in the process of epitaxy of thin nitride-based quantum structures on foreign substrates, such as sapphire, SiC, or Si. This significantly reduces the quality and performance of the devices because of lattice constant and thermal expansion coefficient mismatch between the device structure and the substrate. However, there is a growing interest in replacing the foreign substrates with bulk GaN ones. This is especially important in the case of high-power electronic components, which require high operating voltages, and lasers with high optical power. The technology to obtain bulk GaN substrates is difficult and their availability on the market is limited.

Poland is one of the leaders in the fabrication of high quality GaN crystals and substrates. Ammonothermal (AT) and Halide Vapor Phase Epitaxy (HVPE) growth technologies are developed at the Institute of High Pressure Physics PAS (IHPP PAS). Main effort will be dedicated to GaN crystals obtained by ammonothermal method (AT-GaN). AT crystallization consists of dissolution of GaN feedstock in supercritical ammonia in one zone of a high-pressure autoclave and its convection-driven transport to the second zone where solution is supersaturated and crystallization of GaN on native GaN seeds takes place. The process is performed at temperature of 450-550°C and ammonia pressure of the order of a few kbars. The method allows to obtain crystals of extremely low threading dislocation density and small bending of crystallographic planes. One of disadvantages of the ammonothermal method is the low purity of the obtained crystals, i.e., a relatively high concentration of point defects (foreign atoms of dopants and structural point defects). HVPE method allows for a fast growth of thick crystals at temperature above 1000°C. Unlike AT-GaN, HVPE-GaN is characterized by high purity, meaning much lower concentration of donor dopants and compensating defects. HVPE-GaN crystals will be used as reference in order to create a more general picture of point defects in bulk GaN

The main unintentional dopant in the AT-GaN crystals is oxygen, which acts as a donor and is the reason of n-type (electron) conductivity. In order to achieve a hole conductivity (p-type), intentional doping with acceptors, such as Mg or Zn, of a sufficiently high concentration is applied. It is also possible to obtain crystals of high resistivity at room temperature (> $10^6$ Ω cm) if the oxygen donors are perfectly compensated by shallow (Mg, Zn) or deep (Mn) acceptors. Preliminary studies indicate that the main defects present in AT-GaN are gallium vacancies, which can additionally bind a maximum of four hydrogen atoms. Such defects may limit the fabrication of crystals with the desired electrical properties, form absorption bands in the visible range or actively participate in optical transitions, e.g., constituting as non-radiation recombination centers.

The goals of the project are: 1) identification of point defects in bulk AT-GaN crystals of various conductivity, 2) impact of the defect concentration on the electrical and optical properties of bulk GaN, and 3) determination of the microscopic mechanism of change of electrical properties after annealing. A complex analysis and determination of concentration of point defects in AT-GaN will be carried out using various experimental methods. The experimental results will be described using calculations based on the charge neutrality equation to obtain a comprehensive image of point defects in bulk AT-GaN.

The project opens an opportunity of studying defect physics in GaN of a wide spectrum of electrical properties (type n, type p, high resistance crystals) and doping level. It will provide a lot of valuable information about the favored conditions of point defect formation, verification of energy level positions known from theoretical calculations, as well as interaction with impurities. It can shed new light on the behavior of defects during post-growth annealing of AT-GaN crystals with a significant concentration of oxygen and gallium vacancies. Especially in AT-GaN doped with acceptors the role of oxygen, hydrogen, Ga vacancies complexed with hydrogen is not well established and dehydrogenation process is not well understood. Thus, an explanation of microscopic change of the defect distribution and resulting resistivity of AT-GaN after thermal annealing will be a measurable success of the project. Knowledge about the type and concentration of point defects in bulk GaN crystals is essential for controlling their purity as well as electrical properties of substrates prepared for specific applications.