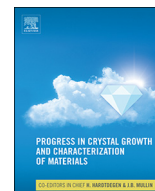




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# Progress in Crystal Growth and Characterization of Materials

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## Basic ammonothermal growth of Gallium Nitride – State of the art, challenges, perspectives

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### ABSTRACT

Recent progress in ammonothermal technology of bulk GaN growth in basic environment is presented and discussed in this paper. This method enables growth of two-inch in diameter crystals of outstanding structural properties, with radius of curvature above tens of meters and low threading dislocation density of the order of  $5 \times 10^4 \text{ cm}^{-2}$ . Crystals with different types of conductivity, n-type with free electron concentration up to  $10^{19} \text{ cm}^{-3}$ , p-type with free hole concentration of  $10^{16} \text{ cm}^{-3}$ , and semi-insulating with resistivity exceeding  $10^{11} \Omega \text{ cm}$ , can be obtained. Ammonothermal GaN of various electrical properties is described in terms of point defects present in the material. Potential applications of high-quality GaN substrates are also briefly shown.

### 1. Introduction

Gallium Nitride (GaN) is a semiconductor with a wide and direct energy gap of 3.44 eV at room temperature [1,2]. The material is famous for its applications in optoelectronic devices operating in a short wavelength region (UV, blue, and green light) [3]. Structures composed of ternary mixed compounds, like InGaN or AlGaN, are commonly used in effective semiconductor light emitting diode (LED) sources, blue and green laser diodes (LDs), as well as UV detectors. Among many advantages of GaN are its high thermal, mechanical, and chemical resistance, as well as high breakdown voltage, high saturation electron velocity and high electron mobility. Such outstanding parameters make GaN attractive for high-power electronics, especially when high reliability at high operating current is required [4,5]. It is expected that technological progress of GaN electronic devices will allow them to compete with commercially available silicon-based ones. Moreover, GaN will push the performance of devices beyond the limits available for other semiconductors, like silicon carbide, silicon, or gallium arsenide [4–7].

At present, commercially available GaN-based electronic and optoelectronic devices are manufactured mainly by heteroepitaxy of nitride quantum structures on foreign substrates (sapphire, silicon carbide, or silicon). This leads to generation of high threading dislocation density (TDD) in the structures, limiting power, efficiency, and lifetime

of the devices. High TDD, in the range  $10^6$ – $10^8 \text{ cm}^{-2}$ , is the reason of strong energy dissipation which narrows the range of operation parameters and limits the device performance. The ideal solution to this problem is using bulk GaN substrates for homoepitaxy. However, due to high melting temperature, exceeding decomposition temperature, bulk GaN crystals cannot be synthesized by standard equilibrium growth methods (like Czochralski method commonly used in production of semiconductor substrates). This is the reason for a limited availability of GaN substrates on the market. The most promising results of thick GaN crystallization were obtained with Hydride Vapor Phase Epitaxy (HVPE) [8]. High growth rate, exceeding  $100 \mu\text{m/h}$  [9], is one of the factors which enable commercial production of HVPE-GaN wafers. However, the crystals still suffer from all disadvantages of using foreign substrates as seeds. After the removal of the seed, free-standing GaN is plastically deformed with TDD of the order of  $10^6 \text{ cm}^{-2}$  [10,11]. Ammonothermal process (growth on native seeds) was proposed to overcome this problem. The aim of this paper is to show the very recent progress in ammonothermal growth in basic solution. Main technological challenges, encountered during multiplication of the crystals, are discussed. Some ways to overcome these difficulties are proposed. Next, basic properties of various types of ammonothermal crystals (n-type, p-type, and highly resistive) are discussed in terms of presence of point defects and their influence on electric properties. Finally, examples of applications of ammonothermal GaN substrates in optoelectronic and

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electronic devices are described, showing the potential of native GaN substrates for optoelectronic and electronic industry.

## 2. Ammonothermal growth of GaN crystals

### 2.1. Basics of ammonothermal process

Ammonothermal technology is an analogue of hydrothermal one, commonly used in industrial production of quartz [12]. The difference is the use of supercritical ammonia instead of water. The idea of ammonothermal growth is the following: metallic gallium (Ga) or GaN, used as feedstock, is dissolved in supercritical ammonia in one zone of a high-pressure autoclave. The dissolved feedstock is then transported to the second zone, where solution is supersaturated and crystallization of GaN on GaN seeds takes place. An appropriate temperature gradient between dissolution and crystallization zones enables the convection mass transport. Some mineralizers are added to ammonia in order to accelerate its dissociation and enhance the solubility of Ga or GaN. Ammonothermal method enables growth of large diameter crystals of high crystalline quality. It is a well-controlled and reproducible process performed at relatively low temperature (a few hundred degrees Celsius) and pressure of a few hundred megapascals. The growth can be proceeded under different environments: basic or acidic. The type of environment is determined by the choice of mineralizers. Ammonobasic growth makes use of alkali metals or their amides as mineralizers ( $\text{NH}_2^-$  ions are introduced into the supercritical solution) [13–15], while in ammonoacidic growth halide compounds are present ( $\text{NH}_4^+$  ions are introduced into the supercritical solution) [16]. High-temperature ammonoacidic growth [17,18] can also be realized by internal heating of the growth chamber (in opposite to external heating of the entire autoclave). This way higher growth temperature and pressure (about 750 °C and 0.6 GPa) than in conventional acidic (500–650 °C, 0.1–0.4 GPa) [16] and basic (400–600 °C, 0.1–0.4 GPa) ammonothermal approach [13] can be achieved by omitting the autoclave material limitations. A negative temperature coefficient of solubility is observed in ammonobasic approach used at Ammono [13]. As a consequence of retrograde solubility the chemical transport of GaN is directed from the low-temperature solubility zone (with feedstock) to the high-temperature crystallization zone (with seeds). It is clearly presented in Fig. 1 which shows a scheme of basic ammonothermal crystallization. The origin of this retrograde chemical transport is still not well understood, despite some detailed investigations on solubility of GaN in ammonia-sodium solutions [19]. In acidic route the process configuration is reversed.

Initial work on basic ammonothermal growth method was performed in the middle of the 1990s [20]. Synthesis of GaN was then realized in supercritical ammonia from metallic Ga at a temperature of 500 °C and pressure of 0.4–0.5 GPa. The resulting crystals were in the form of wurtzite-type microcrystalline powder. Later reports describe synthesis of transparent GaN platelets or prismatic needles with dimensions up to 0.5 mm × 0.2 mm × 0.1 mm in ammonobasic solution [21] and needle-shaped GaN crystals (with diameter up to tens of micrometers and length of hundreds of micrometers) in ammonoacidic solution [22].

In the 2000s a few groups were engaged in ammonothermal method and took advantage of chemical transport in temperature gradient in both environments [23–31]. At present, there are several companies and research institutes working on ammonothermal growth of GaN, such as Ammono (Poland; basic environment), SixPoint Materials Inc. (United States; basic) [32,33], University of California Santa Barbara (United States; acidic and basic) [34–36], University of Stuttgart (Germany; acidic and basic) [37], Mitsubishi Chemical Corp. (Japan; acidic) [16], Tohoku University (Japan; acidic) [38,39], Sora, Inc. (United States; high-temperature acidic) [17,18], Asahi Kasei Corp. (Japan; acidic) [40]. Diameters of ammonothermal GaN crystal were of a few millimeters in 2006–2007 and reached 2 in. in 2010 [15,18, 27].

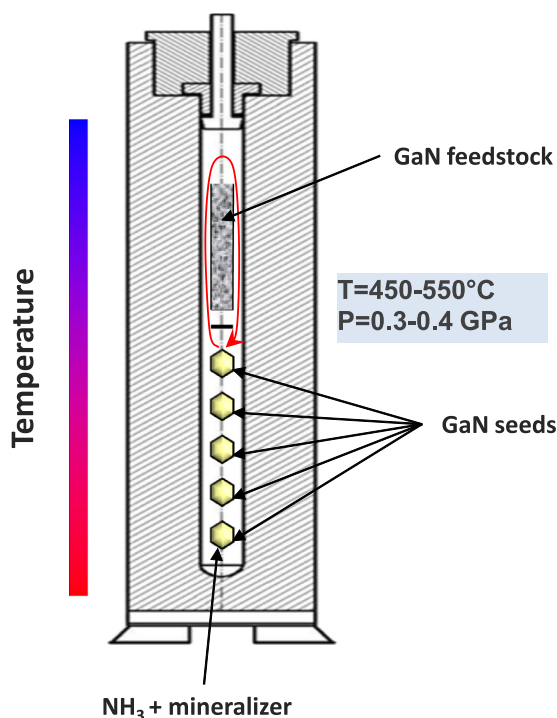


Fig. 1. Scheme of basic ammonothermal process and schematic cross-section of autoclave divided into dissolution zone (with feedstock) and crystallization zone (with GaN seeds). Red arrow symbolizes the convection mass transport in the temperature gradient. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In most of the cited studies HVPE-GaN seeds are still used.

Our version of basic ammonothermal growth proceeds in temperature range 500–600 °C and pressure 0.3–0.4 GPa. The growth is conducted in Ni-based alloy autoclave (material resistant to harsh supercritical ammonia environment) of our own construction. Exceptional structural properties, doping feasibility, and scalability, are the main advantages of this method. In general, growth consists of three stages described below and shown in Fig. 2:

- 1) Stage 1 – Growth of initial native GaN seeds. Our long-term (more than 15 years) experience allowed us to build sufficient stock of GaN seeds of outstanding structural properties: very flat crystal lattice (bowing radius of crystallographic planes higher than 20 m) and TDD of  $5 \times 10^4 \text{ cm}^{-2}$ .
- 2) Stage 2 – Enlargement of seeds. The initial seeds can be gradually enlarged by taking advantage of lateral growth phenomena in non-polar or semipolar directions [41–43], and reach 2 in. or more in diameter [15].
- 3) Stage 3 – Seed multiplication. The final multiplication stage is concentrated on ammonothermal crystal growth in vertical direction mainly (along  $c$ -axis), slicing the crystal perpendicularly to growth direction and increasing the population of seeds used for subsequent growth runs or/and wafering process. We note, that regardless of the seed position in the autoclave, GaN monocrystals can be obtained on all the seeds (in number of few tens per one growth run). The grown crystals can be classified as an appropriate material for seed or substrate fabrication.

### 2.2. Growth rate

The highest growth rate in ammonothermal method takes place in the lateral  $a$ -direction ( $\langle 11\bar{2}0 \rangle$ ) (or in semipolar direction, like  $\langle 11\bar{2}2 \rangle$ ), while the lowest growth rate is in the  $m$ -direction ( $\langle 10\bar{1}0 \rangle$ ) [34,35,44]. Saito et al. published the following total growth rates: 11  $\mu\text{m}/\text{day}$  in the

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