In memory of Professor Robert R. Gałązka

Recent Progress in Crystal Growth of Bulk GaN

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Perfect crystals are the basis of semiconductor technologies. They are also necessary for the experimental verification of fundamental theoretical models.Professor Robert R. Gałązka has always taken this into account in his ground breaking research.

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State of the art in crystallization of bulk GaN is reviewed and discussed. Fundamental physical barriers making crystal growth of GaN difficult are indicated. The Na-flux, ammonothermal and halide vapor phase epitaxy methods are presented as the most advanced and promising ones. The high nitrogen pressure solution approach developed at IHPP PAS is mentioned as a starting point of bulk GaN research.

topics: crystal growth from solution, crystal growth from gas phase, gallium nitride (GaN)

1. Introduction

Nitride semiconductors are the foundation of the optoelectronics industry [1]. Ultra-violet (UV), blue, green, and even red light emitting diodes (LEDs) are fabricated based on gallium nitride (GaN) alloys with indium nitride (InN) and aluminium nitride (AlN). Commonly applied white LEDs consist of blue ones based on InGaN structures with the appropriate phosphor. Laser diodes (LDs), used today mainly in PlayStationTM, are based on InGaN/GaN quantum wells grown on native GaN substrates. Herein, it should be underlined that all commercially available nitride LEDs are fabricated on sapphire (foreign wafers).

Nitride semiconductors also appeared in the electronics industry [2]. High electron mobility transistors (HEMTs), used on a mass scale in chargers, are fabricated from GaN/AlGaN structures deposited on semi-insulating (SI) silicon carbide (SiC) or silicon (Si) substrates [3]. Many academic and industrial centers work today on field-effect transistors (FETs) in GaN-on-GaN technology, thus applying native and highly conducting GaN as substrates. However, bulk GaN growth technology is still a challenge for the semiconductor community. It is well known that GaN cannot be grown from its stoichiometric melt. The nitrogen (N₂) pressure needed for congruent GaN melting is today too high for industrial applications (> 6 GPa) [4]. Gallium nitride is thus crystallized by technologies that require much lower pressure. The first approach that allowed to crystallize GaN single crystals of the highest structural quality was the high nitrogen pressure solution (HNPS) method developed in the 90s of 20th century and the first decade of the 21st century by the Institute of High Pressure Physics of the Polish Academy of Sciences (IHPP PAS) [5]. The crystals were grown from the solution of atomic nitrogen in liquid gallium (Ga) at the temperature of the order of 1450° C and N₂ pressure up to 1 GPa. These first worldwide high quality GaN crystals were used as a reference for the determination of fundamental properties of GaN as well as the first substrates for homoepitaxial deposition of nitride layers and quantum structures [6, 7]. Due to the extreme conditions involved, the HNPS crystallization method was not developed up to an industrial stage, but the technique is successfully applied for the annealing of various materials. The ultra-high-pressure annealing (UHPA) can change such key properties of glasses as hardness, viscosity, density, or fracture toughness e.g. [8–10]. It can also remove implantation damage from ion implanted GaN-based structures, activate the implanted dopants, and enhance their diffusion. At present, the UHPA is being developed for both industrial (implanted GaN based structures for FETs) and scientific (analysis of diffusion processes in GaN) purposes, e.g. [11–13]. For growing bulk GaN, however, other technologies are used today.

In this paper, the recent progress in crystal growth of bulk GaN is shown. Today, there are three main methods for bulk GaN crystallization: (i) sodium flux, (ii) ammonothermal, (iii) halide vapor phase epitaxy (HVPE) and its derivatives such as halide-free VPE as well as oxide VPE (HFVPE and OVPE, respectively). The first two belong to the group of high-pressure solution growth. All these technologies allow to crystallize GaN of diameter larger than 4 inch (for production of 4 inch wafers). The structural quality and electrical properties (determined by the applications of wafers) are, however, various and depend on the method as well as parameters of the crystal growth process, especially the kind of applied seed.

This paper starts with a short description of GaN thermodynamics and the compound's pressure–temperature (p-T) diagram, which is still not fully determined. Next, the already mentioned three crystals growth methods are briefly described. The paper ends with a summary in which challenges and difficulties in bulk GaN growth are presented and shortly discussed.

2. GaN thermodynamics and p-T phase diagram

In 1984, Karpinski et al. [14] determined the p-Tequilibrium curve for the GaN-Ga-N₂ system at temperature and pressure up to 1800°C and 6 GPa, respectively. This result initiated the already mentioned HNPS crystallization method. At the beginning of the 1990s, Grzegory et al. [15] analyzed the thermodynamics properties of GaN and its constituents and explained the role of the use of high N₂ pressure for GaN synthesis. A part of the liquidus curve, thus the nitrogen solubility data resulting from annealing of Ga in N_2 atmosphere in threephase Ga–N₂–GaN equilibrium conditions for the temperature range from 1300°C to 1550°C, was determined [16]. An extrapolation of these experimental data led to estimating the melting temperature of GaN ($\approx 2200^{\circ}$ C), which was close to the value calculated by Van Vechten in the frame of the classical electronegativity theory [17]. A similar value of the melting temperature with corresponding N₂ pressure of 6 GPa was experimentally determined by Utsumi et al. [4]. By using molecular dynamics Harafuji et al. [18] showed, however, that GaN melting temperature should increase with pressure, and at 6 GPa it should reach 3200°C. Porowski et al. [19, 20] studied the GaN–Ga–N₂ equilibrium curve experimentally at pressures of 6–9 GPa. Melting of GaN was not observed up to 3000°C. Moreover, the melting p-T relation, evaluated from the pressure and temperature dependence of the solubil-



Fig. 1. State of knowledge for p-T phase diagram of GaN.

ity of nitrogen in liquid Ga, agreed with the results presented by Harafuji et al. [18]. It was strongly suggested that GaN melts differently than the majority of tetrahedrally bonded semiconductors and, in particular, below 9 GPa the melting temperature increases with pressure. At these conditions, GaN should melt into a liquid with a density lower than the crystal. On the other hand, solid GaN should transform into a metallic liquid with a density higher than the solid upon melting at much higher pressures. The most relevant data on the p-T phase diagram of GaN collected and recently extended in [21] and are presented in Fig. 1.

The result of [21], where the wurtzite (WZ)-rock salt (RS) solid-solid phase transition was studied as a function of pressure and temperature by X-ray absorption spectroscopy in a laser heated diamond anvil cell, is a good guiding point for evaluation and understanding of the full phase-diagram of GaN, including determination of the GaN melting curve, which is still an open question. In particular, it follows from the diagram in Fig. 1 that observation of melting of GaN in its WZ phase can be a challenge because the pressure window for the existence of this phase at high temperature is limited from both low- and high-pressure sides. For low pressures, the limiting factor is the thermal decomposition of the WZ GaN (purple line in Fig. 1), whereas for high pressures, it is a temperature induced WZ-RS phase transition (blue line).

3. Sodium-flux growth method

The main drawbacks of the already mentioned HNPS growth method were the low solubility of nitrogen in liquid Ga (lower than 1 at% at applied temperatures) and slow convection flow of the growth solution (nearly pure Ga of density 6 g/cm³) resulting in a low GaN growth rate ($\sim 1-2 \ \mu m/h$ in the $\langle 0001 \rangle$ crystallographic direction). In order to increase the solubility and accelerate the convection flow and, thus, the growth rate (by using the lighter solution) sodium (Na) was added to Ga. The



Fig. 2. Scheme of Na-flux crystallization process (see description in text).

method was started at Tohoku University and later was developed at Osaka University, see, e.g. [22–24]. Today, the Na-flux GaN crystallization is performed at N_2 pressure lower than 5 MPa and constant temperature of the order of 1000°C. Sodium increases the solubility of atomic nitrogen in the Na–Ga flux to a few at.% [24]. There is much more Na than Ga in the solution, 73% and 27%, respectively. Nitrogen molecules dissociate on the surface of the flux and dissolve into it. The mass transport is governed by convective flow caused by the mechanical stirring of the flux [24]. The supersaturation is created by the difference between a prevailing N_2 pressure and an equilibrium one for the considered phases of the flux (Na/Ga–GaN–N₂). The GaN crystal is deposited mainly on foreign seeds (GaN/sapphire template) in the (0001) crystallographic direction with a growth rate reaching 20 μ m/h. A template is patterned into GaN point seeds (up to 1 mm in diameter) [25]. Pyramidal islands thus form at the beginning of the growth process. Once the GaN pyramidal islands are developed the seed is pulled out from the solution to switch the growth to a layer by layer mode. At this stage, the Na–Ga solution remains only between the pyramids, and the lateral growth is then enhanced. There is a small amount of the Ga–Na solution between the pyramids. Therefore, the template should be again dipped into the solution. The pulling up and dipping procedures are repeated until the GaN surface becomes flat. Then, the crystallization is continued to obtain a few millimeters thick GaN layer. The initial part of the grown crystal containing the 3D islands should be removed because it is non-uniform in terms of incorporation of impurities. The incorporation on the side facets of the pyramids is different than on the main (0001) growth surface. Due to this fact, differences in the lattice parameters can be observed and, therefore, stress can be generated. While stress may be helpful in separating the crystal from the sapphire substrate, it is unwanted in the material from which the substrate will be prepared. The point seed technique of Na-flux GaN growth described above is schematically presented in Fig. 2.

The Na-flux technology already allowed to demonstrate 6 inch GaN crystals of high structural quality with low threading dislocation density (TDD $\approx 10^4 \text{ cm}^{-2}$) and flat crystallographic planes as well as of high purity [25, 26]. The free carrier concentration is not higher than 10^{16} cm^{-3} in an undoped material. The main donor is oxygen. Germanium (Ge) is intentionally incorporated in order to obtain highly conductive n-type crystals. There are no reports about SI material.

The Na-flux method seems to be a perfect technology for fabricating seeds for further growth of GaN but not for mass production of substrates [27]. It was already demonstrated that Na-flux–GaN can be applied as a seed for another bulk crystal growth approach, i.e, the HVPE gas phase method. The first results presented by the SCIOCS company and Osaka University were promising. The HVPE-GaN crystal of high structural quality, crystallographically flat and with low TDD ($\sim 10^5$ cm⁻²), was reported [28].

4. Ammonothermal growth method

Gallium nitride crystals of the best structural quality can be grown by the ammonothermal method in a supercritical ammonia (NH₃) solution inside high-pressure autoclaves at temperatures of $300-750^{\circ}$ C and pressure up to 0.6 GPa [29, 30]. The idea of the ammonothermal process is the following GaN, used as feedstock, is dissolved in supercritical ammonia in one zone of a high-pressure autoclave. The dissolved feedstock is transported to the second zone, where the solution is supersaturated (higher concentration of reactants than the equilibrium ones) and crystallization of GaN on native seeds takes place. An appropriate temperature gradient between dissolution and crystallization zones enables convective mass transport. Some mineralizers are added to ammonia in order to enhance the solubility of GaN. Thus, the ammonothermal growth can proceed under different environments, i.e, 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, while in ammonoacidic growth halide compounds are present [31]. The schemes of ammonothermal autoclaves for basic and acidic crystallization runs are presented in Fig. 3.

It was noted that very few data on the GaN solubility with the basic sodium amide $(NaNH_2)$ mineralizer can be found in the literature [32]. The best, in terms of structural quality, and the largest, in terms of thickness and lateral size, crystals (see Fig. 4) are grown by the basic ammonothermal method with NaNH₂ as the mineralizer and in a regime of retrograde GaN solubility decreasing with increasing of the temperature [33, 34].

At present, there are several companies and research institutes that work on ammonothermal growth of GaN, such as IHPP PAS, SixPoint

TABLE I

Electrical properties (measured using a home-built Hall effect system in van der Pauw configuration) of three types of ammonothermally grown GaN crystals, at room temperature.

Material type	Conductivity type	$\begin{array}{c} \text{Carrier} \\ \text{concentration} \\ [\text{cm}^{-3}] \end{array}$	$\begin{array}{c} \text{Carrier} \\ \text{mobility} \\ [\text{cm}^2/(\text{V s})] \end{array}$	Resistivity $[\Omega \ {\rm cm}]$
high carrier concentration	n-type	$\sim 10^{19}$	~ 150	10^{-3}
low carrier concentration	n-type	$\sim 10^{18}$	~ 250	10^{-2}
high resistivity manganese (Mn)-doped	semi-insulating	_	_	$\geq 10^8$



Fig. 3. Schemes of temperature distribution and reactors for GaN crystallization by ammonothermal methods: (a) basic and (b) acidic.



Fig. 4. GaN crystals grown at IHPP PAS with the basic ammonothermal method with NaNH₂ mineralizer and by applying a retrograde solubility mode.

Materials Inc. (USA), University of Stuttgart (Germany), Mitsubishi Chemical Corp. (Japan), Tohoku University (Japan), Nagoya University, or Kyocera (formerly Soraa, Inc., USA/Japan) [35–38]. A complete compendium of knowledge on the ammonothermal crystallization process can be found in [39].

The approach used at IHPP PAS is a basic ammonothermal growth process that proceeds in the temperature range 300–550°C and pressure 0.25–0.4 GPa. The growth is conducted in Ni-based alloy autoclaves of own design and construction. Gallium nitride crystals are used as seeds. The growth proceeds in the $\langle 000 - 1 \rangle$ and/or $\langle 11 - 20 \rangle$ crystallographic directions (for details, see [34]). The typical growth rate in the $\langle 000 - 1 \rangle$ direction does not exceed 4 μ m/h.



Fig. 5. Ammonothermal GaN substrates prepared at IHPP PAS (a) n-type wafer with a carrier concentration of 10^{19} cm⁻³, (b) n-type wafer with a carrier concentration of 10^{18} cm⁻³, (c) semi-insulating wafer doped with Mn; grid line 1 mm.

Three types of GaN crystals, in terms of electrical properties, are grown by the basic ammonothermal process at IHPP PAS (see Table I). All of them exhibit excellent, one of the highest on a global scale, structural quality. Their crystallographic planes are flat (bowing radius is higher than 15 m), and the threading dislocation density is of the order of 5×10^4 cm⁻². Figure 5 presents three GaN substrates obtained by wafering procedures (slicing, orientation, dicing, grinding, lapping, mechanical and chemo-mechanical polishing) of crystals with properties listed in Table I. Other structural, electrical, optical, and thermal properties of the ammonothermally grown GaN crystals can be found in the literature (e.g. [40–43]).

5. Halide vapor phase epitaxy and two derivative methods

A scheme of a horizontal HVPE reactor is presented in Fig. 6. In the low-temperature zone of the reactor (800–900°C), hydrochloride (HCl) reacts with Ga to form gallium chloride (GaCl). Gallium chloride is transported by the carrier gas (N₂, H₂, or their mixtures) to the zone where GaN is crystallized due to a reaction of GaCl with NH₃ (flown separately) at 1000–1100°C. The difference between the equilibrium partial pressure of GaCl and a real



Fig. 6. Scheme of a horizontal HVPE-reactor. Here, GaCl is transported to the reaction zone through special nozzles, NH_3 is supplied by a nozzle placed on the same level as a susceptor, CG is carrier gas.

input partial pressure of GaCl at a given temperature of the growth run and NH_3 flow, creates supersaturation, the driving force for crystallization. Gallium nitride can be grown on native or foreign seeds. In the latter case, GaN/sapphire templates or GaAs substrates are mostly used [44, 45]. The main crystallographic growth direction in HVPE-GaN technology is the $\langle 0001 \rangle$ direction.

Crystallization of GaN by the HVPE method in the $\langle 0001 \rangle$ direction has two significant advantages over other methods, i.e, high growth rate and high purity of the material [46–48]. The average rate can be even higher than 100 μ m/h. The new-crystallized GaN can be of high purity, with some unintentional dopants deriving from the reactant gases or solid elements of the reactor. The highest purity GaN was obtained by Fujikura et al. [46]. The overall concentration of unintentional impurities was lower than 10¹⁴ cm⁻³. Doping processes, with Si or Ge for obtaining highly conductive crystals or with iron (Fe), carbon (C), or Mn for semi-insulating ones, are well developed in HVPE and were described in details, e.g. in [49–53].

As mentioned, there are two derivative growth methods to HVPE. In both, HCl is not applied. Thus, there is no corrosive environment in the reactor. Therefore, the elements of the reactor, as well as the gas lines (capillaries, valves, etc.) are not etched by HCl. Additionally, no solid by-products, such as ammonium chloride (NH₄Cl), are produced. In HFVPE (the HCl Free VPE) pure Ga is applied as a precursor. High purity GaN can be grown in the $\langle 0001 \rangle$ direction with a reasonable rate of up to 200 μ m/h. This method is developed mainly at Toyota R&D Laboratory and Nagoya University [54, 55]. The second derivative technology, OVPE (the Oxide VPE), is based on using gallium oxide (Ga_2O) as the Ga precursor. Gallium oxide gas is synthesized by the oxidation of liquid Ga with H₂O vapor. Gallium nitride is crystallized due to a reaction between Ga_2O and NH_3 . The growth rate in the (0001) crystallographic direction can reach 100 μ m/h. The biggest advantage of this method is the possibility to fabricate GaN crystals of extremely low resistivity of the order of $5 \times 10^{-4} \Omega$ cm, due to the incorporation of a large amount of oxygen donor impurities. This method is being developed at Osaka University and Panasonic [56, 57].

HVPE is the most popular method used for producing GaN substrates. Main HVPE-GaN wafers suppliers are: SCIOCS by Sumitomo Chemical [58], Mitsubishi Chemical Corp. [59], Sumitomo Electric Industry [60] from Japan, as well as Nanowin and Eta Research from China [61, 62]. GaN substrates are produced from free-standing (FS) HVPE-GaN crystals, usually grown on foreign seeds. As mentioned, HVPE-GaN deposition on a foreign foundation allows obtaining large diameter GaN crystals. Unfortunately, their crystallographic planes are seriously deformed (bent). This is due to the huge differences between the lattice constants and thermal expansion coefficients of the foreign substrates and the nitride layers. When the 2 inch GaN is grown on sapphire, the value of bowing radius of crystallographic planes is often of the order of 5 m. The crystals can also be plastically deformed and have dislocation bundles [63]. Due to the bowing, it is impossible to orient the substrates uniformly across the entire surface. Uniform orientation is a critical requirement for further epitaxial growth process (device fabrication). The way to overcome this problem is to use native GaN crystals of high crystallographic quality as seeds for the HVPE growth. It enables to deposit GaN with a low TDD ($\leq 10^5 \text{ cm}^{-2}$) and flat crystallographic planes. As already mentioned, Na-flux GaN crystals can be used as seeds. Ammonothermal GaN can also play this role, as was demonstrated by IHPP PAS and Mitsubishi Chemical [64, 65]. Growth of HVPE-GaN on seeds of the highest structural quality helped to reveal the main factor hindering bulk growth of GaN, which is described in the next subsection.

6. Challenges and difficulties of bulk GaN growth

For many years it was assumed that it would be possible to grow truly bulk GaN if the crystallization process was realized on a native seed of the highest structural quality. However, it turned out to be extremely difficult. After exceeding a certain critical thickness of the growing crystal, the appearance of cracks and their propagation in the material was always observed [66, 67]. Obtaining a thick GaN boule was limited by the anisotropy of the growth process in terms of physical properties in sectors of the crystals growing in different directions. The lateral growth on the side facets of orientations other than the normal growth plane causes stress at the edges of the growing bulk crystal due to different incorporation of impurities on different crystal planes [68]. If just one crystal surface can be stabilized and grown for an arbitrary period of time, the



Fig. 7. (a) HVPE-GaN crystallized with a ring of Mo around it; side facets are visible; grid 1 mm. (b) Ammonothermal GaN crystallized with a metal border.

lateral growth should be prevented. In the case of HVPE, it can be achieved by placing metal elements (e.g. molybdenum Mo) at the edges of the growing crystal or around it [69]. Molybdenum catalyzes the decomposition of NH_3 . Then the supersaturation is drastically reduced at the edges of the growing crystal. The crystallization in lateral directions is thus stopped. The crystal can be grown much thicker without the formation of cracks. The side facets are, however, formed. That leads to a reduction of the surface of the growing crystal. The main issue is to find such growth conditions that will allow to form only the side facets that grow faster than GaN in the vertical direction. Then, the side facets will disappear. The crystal will grow in a chosen vertical direction without the reduction in the size of its growing surface.

In the case of the ammonothermal process, the growth in directions other than the selected one can be blocked mechanically with the metal barriers prepared from chosen metals [70]. Native seed is then wrapped with a metal foil and, therefore, the possibility of lateral growth is blocked. At the same time, metal borders that define the shape and height of a newly-grown crystal are built. The metal borders are as high as the planned thickness of the newly-grown material. The growing crystal takes the shape defined by the borders and only can grow in one, well defined, crystallographic direction. When the crystal becomes thicker than the metal borders the facets can form. However, they do not appear because the crystal growth process ends at this moment. Figure 7 presents thick HVPE and ammonothermal GaN crystals obtained using the described above solutions.

7. Conclusions

Physics and technology of GaN developed over the past two decades in a revolutionary way, bringing more and more new technological breakthroughs, for which GaN-based LEDs were awarded the 2014 Nobel Prize in Physics. Nevertheless, there are still essential problems in the physics of GaN to be solved. In particular, the p-T phase diagram including the melting curve of GaN is still not established.

The development of an efficient method for growth of high quality bulk crystals is also an "open question" as physical properties of semiconductor materials are determined to a large degree by the occurrence of various structural and point defects. Due to extreme melting conditions, GaN cannot be grown from its stoichiometric melt by Czochralski or Bridgman methods. Therefore, the crystals have to be grown at pressures and temperatures much lower than is expected for melting. The most advanced method for growing GaN is halide vapor phase epitaxy allowing GaN crystallization with relatively high rates exceeding 100 μ m/h. The highest structural quality GaN single crystals are being grown by ammonothermal method, with the use of supercritical ammonia (NH_3) as a solvent for GaN, at pressures of 0.2–0.3 GPa and 600–800°C. A drawback of this method is a low rate of growth $(2-4 \ \mu m/h)$ and relatively low purity. Nevertheless, the existing methods were developed to a stage sufficient for industrial production of GaN based laser diodes using 2 inch substrates. For GaN-on-GaN vertical power electronics, an increase of substrate diameter up to at least 4 inch is required. The ammonothermal method, despite its limitations, is scalable in terms of both production efficiency and crystal size.

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