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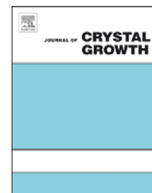

Bulk ammonothermal GaN

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ABSTRACT

In this work, results of structural characterization of high-quality ammonothermal GaN are presented. Besides expected low dislocation density (being of the order of $10^3\,cm^{-2}$) the most interesting feature seems perfect flatness of the crystal lattice of studied crystals. Regardless the size of crystals, lattice curvature radius exceeds 100 m, whereas better crystals reveal radius of several hundred meters and the best above 1000 m. Excellent crystallinity manifests in very narrow X-ray diffraction peaks of full-width at half-maximum (FWHM) values about 16 arcsec.

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1. Introduction

At present, next generation of high-efficiency lighting and high-power electronics are considered as one of the tasks for innovation technologies for energy saving in world industry. In this context, gallium nitride (GaN) has attracted a great attention for its material properties that are useful for applications in short-wavelength optoelectronic and high-power electronic devices [1,2] such as white or colour light-emitting diodes, blue laser diodes, UV detectors, high-power and high-frequency transistors. However, the currently available devices use GaN deposited by heteroepitaxy on sapphire or SiC. Therefore, the resulting thin films suffer from large defect concentrations, mainly due to the difference in lattice parameters and thermal expansion coefficient between such non-native substrates and GaN. Although much progress has been done in fabrication of blue laser diodes by heteroepitaxy in the recent 10 years, the development of low-cost optoelectronic and high-temperature electronic devices of sufficiently high efficiency is limited due to a lack of suitable substrates for growing homoepitaxial structures. In this situation, the growth of bulk GaN has become a big challenge and actual hot topic among GaN researchers. An open question is which technique of GaN substrate production will dominate the market. In this communication, we present ammonothermal method with reference to the other techniques: high nitrogen pressure (HNP) method, Na flux, hydride vapor-phase epitaxy (HVPE).

At present the most common technique used in commercial scale is hydride vapor-phase epitaxy, due to reasonably high growth rates ($100–500\,\mu m\,h^{-1}$ along the *c*-axis) [3]. This method consists of an epitaxial growth employing halides in vapor phase and results in a few millimeter thick crystalline GaN layer. Although blue laser diodes deposited on HVPE substrates are available commercially, the resulting structures still suffer from large dislocation density generation and the problem of parasitic nucleation of HVPE layers exceeding about 100 µm in thickness [3]. The first problem is a direct consequence of use of non-native substrates (sapphire or GaAs), separated after the growth by, for example, laser-induced lift off. Obtained this way, quasi-bulk GaN is still highly stressed and the resulting freestanding GaN wafers are highly bowed. In this respect, high-quality GaN wafers production by HVPE for optoelectronics raises more and more questions and doubts.

An ideal solution to the problem would be growth of truly GaN crystals which seems to be a very difficult task, since standard methods of crystallization from the melt (Czochralski, Bridgman) and sublimation are not applicable because of the decomposition of the nitrides into metals and N_2. In the HNP method, this decomposition is inhibited by the use of nitrogen under high pressure [4]. The growth of single crystals is performed in molten gallium and requires temperatures of about 1500 °C and nitrogen pressures in the order of 15 kbar. Besides the extreme growth conditions, the main disadvantage of this method is relatively low crystal size not exceeding 20 mm [5].

Another approach to bulk GaN growth is a process using Na flux [6]. It consists of the thermal decomposition of sodium azide (NaN_3) and the reaction between created this way nitrogen with

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gallium. The process takes place at temperatures 300–800 °C and pressure ranging from atmospheric to few MPa. Sodium is regarded as a catalyst that enables N_2 dissociation. Although 2-inch-size wafers were achieved by means of sodium flux liquid-phase epitaxy (Na flux-LPE) [7], grain structure is easily visible, and the factors like expensive solvents, low yield (one crystal per growth process), low controllability of the process and the limited scalability may hamper real mass production of bulk GaN crystals by this method.

2. The ammonothermal method

We propose the ammonothermal technique with the help of which one can overcome the aforementioned obstacles. Firstly, it enables to grow high-diameter seeds with perfect crystalline quality. Secondly, it is very well controllable and reproducible process at relatively low temperatures and pressures. Thirdly, it enables excellent scalability with the size of the autoclaves and growing many crystals during one process with minimized material costs (closed system).

The idea of the ammonothermal technique was inspired from the field of hydrothermal technology, used commercially in quartz mass production [8] (tens of tons per year are produced with the cost of few dollars per kilogram), where supercritical aqueous solutions are used for recrystallization of oxides. The ammonothermal method is regarded as an analogue of hydrothermal one, where ammonia instead of water is used as a solvent and nitrides can be grown instead of the oxides. The typical temperatures and pressures applied are 400–600 °C and 0.1–0.3 GPa, respectively. The scheme of the crystal growth process is the following: GaN containing feedstock is dissolved in one zone of the high-pressure autoclave, then transported by convection in the temperature gradient to the second zone, where GaN is crystallized on native seeds due to the supersaturation of the solution (Fig. 1). In addition, the use of the mineralizers is necessary in order to enhance the solubility of GaN in ammonia. They can introduce NH_2^- ions to the solution in case of ammonobasic environment of ammonothermal growth, NH_4^+ ions in case of acidic environment or they can supply neither of them in the case of neutral environment.

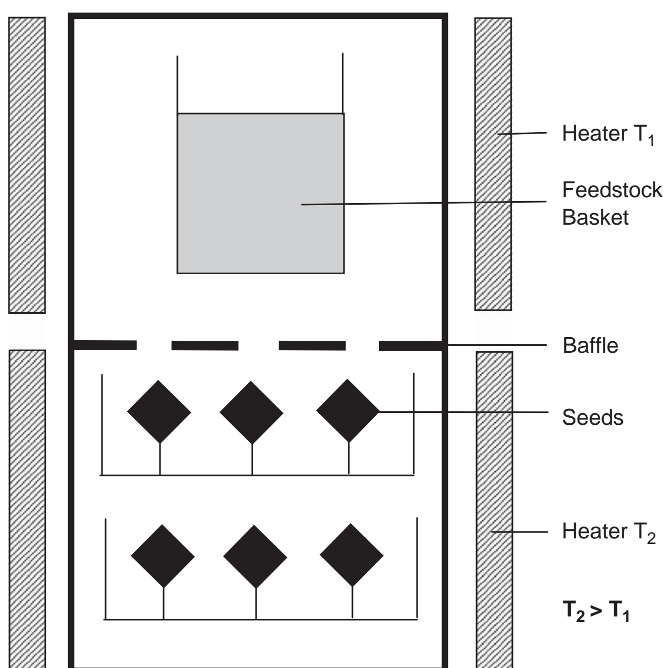

Fig. 1. Schematic idea of the AMMONO-Bulk method.

The first reports on ammonothermal growth of GaN appeared in the middle of the 1990s [9,10]. GaN syntheses were then realized in supercritical ammonia from metallic gallium, at a temperature of 500 °C and pressure 400–500 MPa. A mineralizer in the form of lithium or potassium amide was added into the reaction zone. However, since the growth was conducted spontaneously without any chemical transport, the resulting GaN crystals were in the form of wurtzite-type microcrystalline powder. On the other hand, very sharp peaks of near band-edge emission accompanied with diminishing of yellow band was observed for samples grown with addition of rare earth elements [11], which suggests high affinity of rare earths to oxygen atoms, yielding to reduced free electron concentration [12].

At the end of the 1990s Kolis et al. [13] performed crystal growth of GaN in ammonobasic conditions using ammonia as solvent and gallium nitride as a nutrient in the temperature T=400 °C and pressure p=240 MPa. They obtained transparent GaN platelets or prismatic needles up to $0.5 \times 0.2 \times 0.1\,mm^3$ [14] thanks to mineralizers such as sodium or potassium amide with the addition of co-mineralizer (MX, M=Li, Na, K and X=Cl, I). In acidic medium, the ammonothermal synthesis from metallic gallium with ammonium halcogenide (NH_4X, X=Cl, Br, I) leads to a zinc-blend-type (cubic) GaN powder [15] or coexistence of hexagonal and cubic phases, depending on the growth temperature. The growth was performed at initial pressure of 70 MPa and thermal gradient 10 °C/cm during heating in the quartz tube. Needle-shaped GaN crystals (with diameter up to few tens of μm and length of several hundreds of μm) were also obtained [16] by recrystallization of GaN using NH_4Cl mineralizer at T=500 °C and relatively low pressure p=120 MPa.

At present, much progress has been done in enlargement of size of the ammonothermally grown crystals taking advantage of chemical transport in temperature gradient. Few groups have presented some important results on GaN synthesis by fluid transport both in ammonobasic [17–23] and ammonoacidic [24–26] conditions. In 2006, Wang and Callahan [20] have demonstrated single GaN crystals of $\leqslant 10 \times 10 \times 1\,mm^3$ in size using GaN as a nutrient. Spontaneously nucleated precipitates (of maximum size being 10 μm) on GaN seeds were observed by Hashimoto et al. [21] if metallic Ga is used as a nutrient in dissolution zone. D'Evelyn et al. [23] have succeeded in growth of mm-sized nucleated GaN crystals on HVPE seeds by fluid transport in the high-pressure ammonothermal method. They described their progress in reduction of impurity concentrations, wafering and even fabrication of homoepitaxial laser diodes on ammonothermal GaN substrates. Recently, uniform growth of thick GaN via fluid transport on a $3 \times 4\,cm^2$ HVPE oval-shaped substrate [27] by ammonobasic route and about 0.5-mm-thick single-crystalline GaN crystal on 1-inch-large HVPE seed by ammonoacidic [28] one are presented.

The ammonobasic version of the ammonothermal method presented in this paper was invented and highly developed at the AMMONO company in collaboration with Nichia Corporation since the beginning of 2000s [17,18]. The inventors observed a non-standard negative temperature coefficient in this route for the first time [17,19]. The consequence of a negative temperature coefficient is that the chemical transport of GaN is directed from the low-temperature solubility zone (with feedstock) to the high-temperature crystallization zone (with seeds) which must be located below the solubility zone of the autoclave. This limits the number of impurities and alien crystal phases, which typically tend to crystallize in the cold end (solubility zone) of the autoclave chamber. Besides the negative coefficient, the

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