Excellent Crystallinity of Truly Bulk Ammonothermal GaN

Gallium Nitride (GaN) has attracted a great attention for its material properties that are useful for applications in short-wavelength optoelectoelectronic and high power electronic devices such as white or color light emitting diodes (LEDs), blue laser diodes (LDs), UV detectors and high power-high frequency transistors [1]. However, the currently available optoelectronic and electronic devices are manufactured mainly by heteroepitaxial methods, in which a variety of substrates, different than GaN, is applied, including sapphire, silicon carbide, silicon, zinc oxide, and many others [1]. The well-known disadvantages of heteroepitaxy are: lattice mismatch, thermal-expansion-coefficient difference, and/or chemical incompatibility, which in effect lead to nitride epilayers with high stress, high dislocation density, and mosaic crystal structure. This limits seriously the lifetime and power of aforementioned devices. During the past decade, an enormous effort was put into overcoming these fundamental obstacles, and an impressive progress was done, especially in high-efficiency LEDs or LDs manufacturing. However, it is widely expected that even these highly-engineered devices can benefit from the use of native (i.e. GaN) substrates and bring real technological breakthroughs.

At the moment, the main source of GaN substrates is the HVPE technique which is advantageous from the point of view of high growth rate, and yields crystalline GaN layers of a few millimeter thickness. However, this method by its own suffers from all disadvantages of heterogeneous (sapphire) substrates on which the growth is initiated. Even after removal of non-native substrate the thus-obtained free-standing GaN layer is highly stressed, and the resulting GaN wafers are typically highly bowed.

An ideal and ultimate solution to the problem are GaN substrates sliced from truly-bulk GaN crystals. Due to a high covalency and an extremely high decomposition pressure at the melting point it is not possible to grow GaN by standard melt-growth method. Therefore, many growth methods have been developed, including solution growth from Ga melt, Ga-Na alloys, and a variety of flux-assisted methods, in which the pressures range from atmospheric to as high as 20 kbar. Despite spectacular results and low dislocation density of grown crystals, these techniques suffer from relatively low dissolution of GaN in the melt, low controllability of the process, difficulties in implementing seeds, and limited scalability.

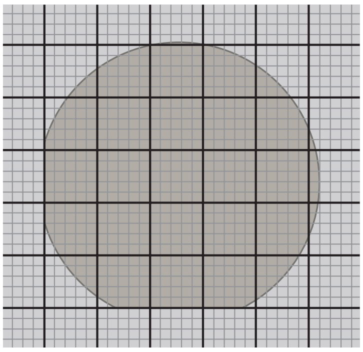

Fig. 1. 1-inch AMMONO-GaN substrate.

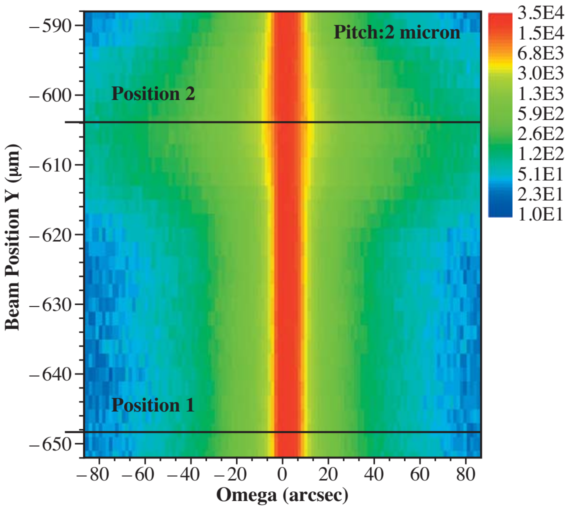

Fig. 2. X-ray micro-beam Omega-scan map for a 2-µm pitch.

The ammonothermal method is a straightforward counterpart of hydrothermal technology, used in α-quartz commercial production. GaN-containing feedstock is dissolved in supercritical ammonia solution in one zone of the high pressure autoclave, then transported through solution by means of convection, and finally crystallized in the second zone, preferably on GaN seeds. The typical temperatures and pressures applied are 0.1- 0.3 GPa and 500°C – 900°C, respectively. The crucial point is the choice of mineralizer – the ionic substance added to the reaction zone in order to increase a reversible dissolution of GaN in ammonia. In the ammonothermal method of growing bulk GaN single crystals, invented, developed and implemented by the AMMONO company in collaboration with Nichia Corporation (AMMONO-Bulk Method), the growth is carried out in so called ammonobasic regime, where the mineralizer introduces NH_2^- ions to the solution. Our team has showed for the first time negative temperature coefficient of solubility $(\partial S/\partial T|_p < 0)$ in ammonobasic environment [2,3]. As a consequence, the chemical transport of GaN is directed from the low-temperature zone of the autoclave to the high-temperature zone. Furthermore, as convection is a driving force for the mass transport, one has to place the high-temperature zone (with seeds) below the low-temperature zone (with feedstock) in order to obtain an efficient re-crystallization.

In general, the main benefits one can gain from application of ammonothermal method are: (i) the possibility of growing high-diameter seeds with excellent structural properties, (ii) repeatable and highly controlled re-crystallization process at close-to-equilibrium conditions (this enables, upon

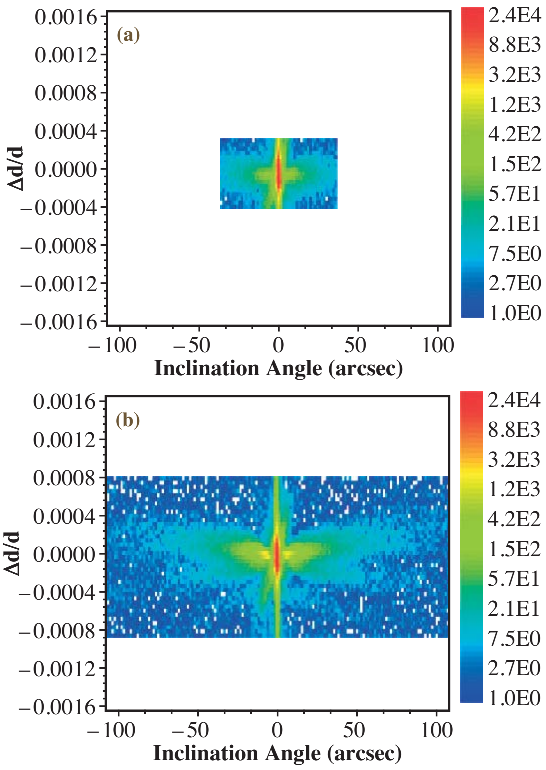

Fig. 3. X-ray micro-beam reciprocal-space maps. **(a)** Position 1; **(b)** Position 2.

request, either dissolution or crystallization of seeds by simple change of thermal conditions), (iii) relatively low growth temperatures, and (iv) excellent scalability of the process with the size of autoclaves. Moreover, as the long-duration processes are possible, one can grow large crystals and slice them in arbitrary directions (*c*-, semi-polar or non-polar planes).

Since the AMMONO-Bulk Method enables growth of high-quality seeds that can be further multiplied and re-grown without a noticeable loss of quality, the AMMONO-GaN crystals are characterized by excellent structural properties. In Fig. 1 we introduce a typical 1-inch AMMONO-GaN substrate, i.e., an oriented and polished wafer which was sliced from a larger AMMONO-GaN crystal. All structural data shown below were measured on as-grown AMMONO-GaN crystals of various shapes and dimensions which did not influence their properties.

The pure hexagonal phase of ammonothermally grown GaN was confirmed by powder diffractometry of pulverized crystals [3]. Excellent crystalline quality was confirmed by the Synchrotron Radiation Microbeam (SRM) measurements on the (0002) plane. Such investigations were performed by means of the synchrotron radiation SPring-8 facility, at beamline **BL24XU**. An AMMONO-GaN sample was scanned along the [11-20] direction with the 0.76 μm × 30 μm X-ray beam. As a result a set of rocking-curve maps was obtained. For example, in Fig. 2 a 60 μm-range scan with a 2 μm pitch is demonstrated. Then, two positions were chosen in which the widths of rocking curves were relatively lower (Position 1) and higher (Position 2). In these two positions, structural properties of AMMONO-GaN were illustrated by reciprocal-space maps, as shown in Fig. 3 where (a) corresponds to the Position 1, and (b) corresponds to the Position 2. In both cases, the general conclusion is that AMMONO-GaN crystals reveal excellent single-crystal structure, without mosaicity and low-angle grain boundaries.

Rocking curves measured for a number of AMMONO-GaN samples (#1-#4) are shown in Fig. 4. Thanks to high monochromaticity, excellent collimation, and a very low diameter of the X-ray microbeam, the FWHM values of rocking curves of the level of 10 arcsec was achieved. Perfect crystallinity was also manifested by large radius of curvature (higher then 1000 m in the best crystals) and low dislocation density (below 10^4 cm^{-3}) [3].

The excellent structural properties of crystals (FWHM value of X-ray rocking curve of about 10 arcsec), combined with advantages of the method itself (seed-multiplication, repeatability, scalability), allow us to claim that AMMONO-Bulk Method is an extremely promising technology for fabricating high-quality, large diameter GaN substrates. Moreover, high scalability of the method will play a crucial role in further improving its cost-effectiveness when implemented in the industrial scale.

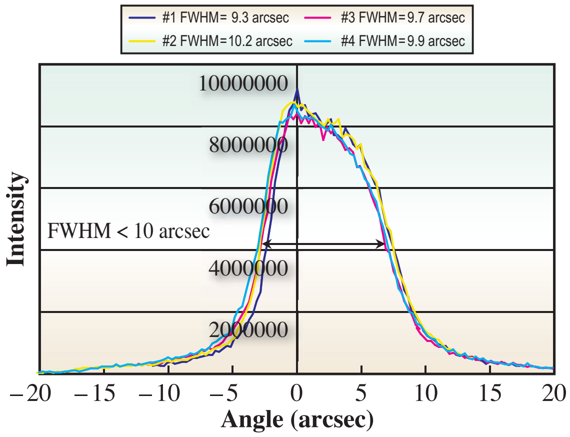

Fig. 4. X-ray microbeam rocking curves for AMMONO-GaN.

Robert Dwiliński[a,*], Marcin Zając[a] and Yasuo Kanbara[b]

[a] Ammono Sp. z o.o., Poland
[b] Nichia Corporation

*E-mail: dwilinski@ammono.com

References

[1] S.C. Jain *et al.*: J. Appl. Phys. **97** (2000) 965.
[2] R.T. Dwiliński *et al.*: United States Patent no. 6,656,615 B2 (02.12.2003).
[3] *R. Dwiliński, R. Doradziński, J. Garczyński, L.P. Sierzputowski, A. Puchalski, Y. Kanbara, K. Yagi, H. Minakuchi, H. Hayashi: J. Crystal Growth* ***310*** *(2008) 3911.*