Low dislocation Gallium Nitride substrates for space applications

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Abstract

This paper summarises the results of the “Low dislocation GaN substrates for space applications” project (contract no. 4000108320/13/NL/KML). The goal of this project was to obtain two-inch semi-insulating Gallium Nitride substrates (of resistivity not lower that $10^5\ \Omega$ cm) of very low dislocation density by ammonothermal method. High resistivity was achieved due to a compensation of unintentional oxygen donors (of concentration 1×10^{18} cm^{-3}) by shallow Mg acceptors. In the project, the 2-inch diameter highly-resistive seeds and crystals were obtained. From these crystals the 2-inch semi-insulating substrates were machined and their surfaces were polished to the epi-ready state. The final parameters (dislocation density 2×10^4 cm^{-2}, lattice curvature radius of several tens of meters, resistivity of at least 10^{11} Ω cm) indicate outstanding structural and electrical quality of this new product.

I. INTRODUCTION

GaN features in high electron mobility, high breakdown voltage, good thermal conductivity and mechanical properties. GaN-based High Electron Mobility Transistors (HEMTs) are characterized by at least one order of magnitude higher power density and efficiency than Si- and GaAs-based conventional devices [1], enabling 10-fold reduction of electronic chip size under the same output power. In this respect, the quest for fabrication methods of native bulk GaN substrates is obvious. In particular, highly resistive GaN substrates are demanded for microwave electronics and devices operating at high voltage (above 1000V). Recently, a large interest has been dedicated to ammonothermal method, which is at present regarded as one of the key technologies for bulk GaN substrates manufacturing. In this paper we will show latest achievement and parameters of semi-insulating GaN substrates of 2-inch diameter, obtained by this method. Such size of a substrate is a minimum one required by electronic industry, manufacturing high-power and high-frequency transistors for microwave applications and many others, including space ones. High resistivity of the substrate is necessary in order to prevent the GaN-based High Electron Mobility Transistors (HEMTs) from parasitic conductivity in substrate/epitaxial structure interface and reduce of the leakage current.

II. AMMONOTHERMAL TECHNOLOGY

Due to high melting temperature, bulk GaN crystals cannot be synthesized by standard equilibrium growth methods (like Czochralski method commonly used in Si and GaAs substrate production), limiting their availability on the market. The most promising results were obtained through the growth of thick layers by Hydride Vapor Phase Epitaxy (HVPE), but the structures deposited on these substrates still suffer from all disadvantages of using heterogeneous substrate, on which the growth was initiated. Even after removal of non-native substrate, the freestanding GaN is still highly stressed and bowed (lattice curvature radius about 1 m) and its dislocation density is still reasonably high (above 10^6 cm^{-2}).

The ammonothermal method can be regarded as an analogue of the hydrothermal one, commonly used in industrial quartz production. In this method GaN feedstock is dissolved in supercritical ammonia solution in dissolution zone of high pressure autoclave, then transported to crystallization one via convection, where crystallization on GaN seeds takes place due to supersaturation of the solution. The crystal growth proceeds in temperature range T=400-600°C and pressure p= 0.2-0.4 GPa. The appropriate temperature gradient between dissolution and crystallization autoclave zones makes convection driven mass transport possible. In addition, the presence of mineralizer is necessary in order to enhance the solubility of GaN in ammonia. In the ammonobasic version of the method, the alkali metals, or their amides ($LiNH_2$, $NaNH_2$, KNH_2), are used as mineralizers introducing NH_2^- ions into the solution. The ammonothermal method enables growth of large diameter crystals of high crystalline quality and is well controlled and reproducible process performed at relatively low temperature. It is a perfectly scalable method (with autoclave size), enabling simultaneous growth of many crystals in one run under minimal material costs. The GaN crystals produced by ammonothermal method (AMMONO-GaN) demonstrate exceptionally low full width at half maximum (FWHM) value of X-ray rocking curve (20 arcsec), large lattice curvature radius (R~100 m) and the lowest dislocation density (of the order of 10^4 cm^{-2}) [2].

III. OBJECTIVES:

The electrical properties of the wafers can be controlled by appropriate doping. Both *n*-type (n~10^{18} - 10^{19} cm^{-3}, $\rho = 10^{-3} \div 10^{-2}$ Ω cm), *p*-type (p~10^{16} cm^{-3}, $\rho = 10^1 \div 10^2$ Ω cm) and semi-insulating (SI) substrates can be grown via ammonothermal method, as measured by both Hall effect experiments and contactless methods. Tuning the electrical properties suggests, that truly bulk A-GaN crystals may find application in both optoelectronics (highly conductive substrates) and high power electronics (SI substrates for HEMT transistors). Standard ammonothermal crystals possess n-type conductivity, due to non-intentional oxygen doping (typical donor dopant in GaN), characterized by the electron concentration of the order of 10^{19} cm^{-3}. Semi-insulating properties was achieved by intentional doping by shallow acceptors, that compensate residual donors [3], yielding homogeneous resistivity in the range ρ~$5x10^{11}$ Ω cm ÷ $7x10^{11}$ Ω cm in case of 1.5-inch diameter substrates.
Recently, substantial progress in the purity (for example by providing getters bounding oxygen from the solution growth) of the ammonothermal process was made, reducing the oxygen concentration by about one order of magnitude (to the level of 10^{18} cm^{-3}). This achievement allowed to decrease the concentration of intentional acceptor, necessary to compensate the AMMONO-GaN crystals and obtain high resistivity material. Such approach was tested with success in small diameter substrates not higher than 1.5-inch. Therefore, taking advantage of scalability of ammonothermal method, the aim of this work is growth of 2-inch semi-insulating substrates of improved purity. The project is divided into few stages, consisting of preparation of highly resistive seeds of sufficient diameter, then growth of 2-inch crystals, out of which the 2-inch semi-insulating epi-ready substrates were fabricated by appropriate crystal machining (slicing, coring, polishing).

IV. RESULTS

In the first step of the project the 2-inch diameter crystal seeds were obtained by lateral enlargement of conductive seeds of smaller diameter (approximately 1.5-inch). The concentration of acceptors was increased gradually in order to avoid possible strain, generated by various concentration of dopants in the seed and the grown crystal. Several growth runs (with the use of getter) were performed to achieve the seed of appropriate size and, simultaneously, final optimization of acceptor concentration was done to achieve high resistivity not only for as-grown crystals, but also for crystals annealed at high temperature used in Metalorganic chemical vapor deposition (MOCVD). Fig. 1 shows the example of such a crystal. Oxygen and Magnesium concentrations were measured by Secondary Ion Mass Spectroscopy (SIMS), yielding about $1.7x10^{18}$ cm^{-3} for both elements.

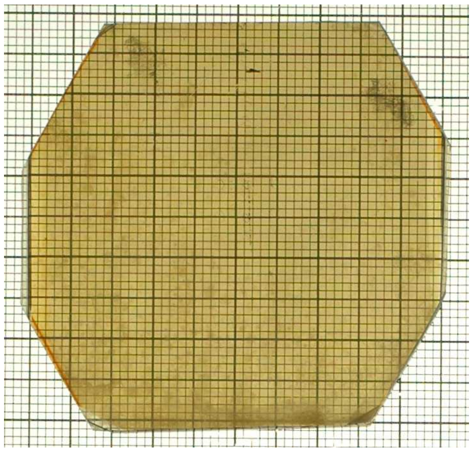

Fig. 1. *Photograph of thick 2-inch highly resisitive crystal obtained by ammonothermal method.*

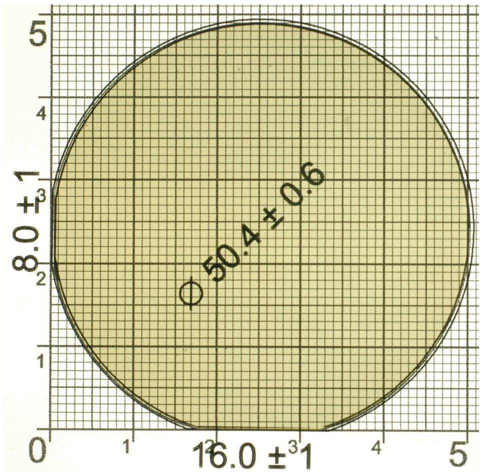

Fig. 2. *Photograph of 2-inch semi-insulating substrate of reduced (to the level of low 10^{18} cm^{-3}) oxygen content obtained by ammonothermal method.*

Obtained crystals were sliced and cored in order to form a circular shape substrate of 2-inch diameter with larger primary flat of (1000) orientation and shorter secondary flat of (11-20) orientation (Fig. 2). The wafers are misoriented with a miscut angle value on demand (typically δ=±0.35° along [11-20]-direction or [1000]-direction]). This allows for epitaxy in 2-dimensional mode, resulting in flat morphology. Further steps of machining require mechanical grinding and then polishing of (0001) surface (Ga-face) – a surface dedicated to epitaxy. Polishing is a multi-stage process, consisting of preliminary mechanical polishing and mechanochemical (CMP) polishing. The latter one is done by using a proper combination of selected chemical etching and mechanical polishing. The aim of CMP should be removal of all scratches, ghosts of scratches and subsurface damage layer (generated during the previous mechanical polishing stages), leading to a smooth surface morphology. The roughness was checked by Atomic Force Microscope (AFM), revealing root mean square (RMS) value of 0.1-0.2 nm, indicating surface quality prepared according to the epi-ready standard.

Measurements of the lattice curvature radius of the AMMONO-GaN and FWHM of rocking curves were performed with the following setup: Cu Kα1 line, U=40kV, I=20mA, 0.1mm ×0.1mm slit and 2mm x 2 mm for the incident beam and an open-detector mode for the diffracted beam. The measurement consisted in collecting of about 10 X-ray rocking curves from (0002) plane, measured in co-linear points spaced by 4 mm along the crystal. A typical result of such a measurement is presented in Fig. 3 for highly resistive 2-inch AMMONO-GaN substrate. Because of the lattice bending, the maxima of diffraction peaks shift systematically on the Ω-axis. This effect reflects the fact that the inclination of (0002) plane changes systematically when moving along the measurement line. When calculating the radius of curvature, the values in the range of 20-200 m were obtained. It is worth to stress that curvature radius is larger than the typical value for HVPE crystals (few meters). The resulting FWHM value is about 20 arcsec, which is an outstanding result for bulk GaN materials. Moreover, this FWHM is repeatable for all the substrates coming from the same process, and its surface distribution (in one crystal) is uniform.

In addition to rocking curves, lattice parameters *a*,*c*, were measured for 2-inch crystals. Those parameters were obtained by making reciprocal space lattice sections for reflexes (0006) and (11-24) and calculating appropriate crystallographic plane spacings d_{hkl}. Obtained lattice parameters are a=3,189106 Å and c=5,18559 Å.

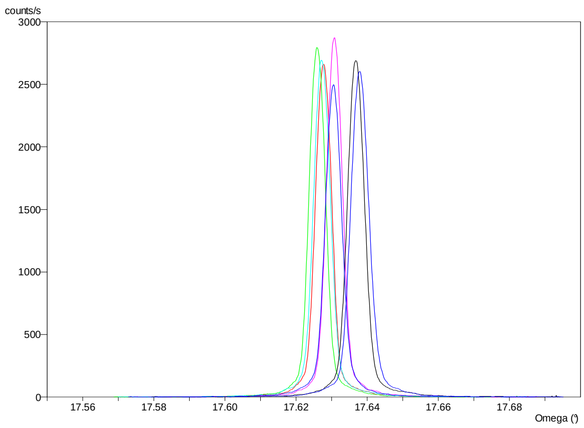

Fig. 2. *Omega-curves measured at collinear points of 2-inch highly resistive substrate, yielding curvature radius of 20-200m and FWHM value of about 20 arcsec.*

The threading dislocation density of 2-inch substrates was investigated by chemical etching of well-polished Ga-face (0001) surface (without subsurface damage leyer) in NaOH/KOH eutectic mixture at temperature 530 °C for 20 minutes. The Nomarski contrast microscope image of such etched surface is shown in Fig. 4. The dislocation density was estimated by calculation of etch pit density (EPD), yielding $2x10^4$ cm^{-2}, which is a typical value for ammonothermal crystals, being well below the competitive bulk HVPE substrates.

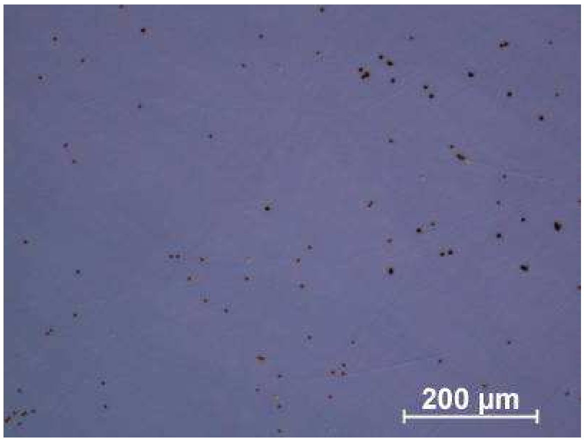

Fig. 4.*Nomarski contrast microscopy image of (0001) face of GaN substrate, revealing the threading dislocation density of $2x10^4$ cm^{-2}.*

Resistivity was measured by capacitance method in frequency domain [4] developped at Faculty of Electronics, Warsaw University of Technology. The idea of this method is the following – it consists of the measurement of capacity of equivalent cuircut of double layer capacitor, containing semiconductor wafer and air (Fig. 5). Simple calculations show that the Q-factor Q=1/(ωRC) approaches minima at certain frequencies that depend on the resistivity of the semiconductor sample and the capacitances C_{sem} and C_0 according to the following equation :

$$f_{\min} = \frac{1}{2\pi R_{sem}\sqrt{C_{sem}(C_{sem}+C_0)}} \qquad (1)$$

In order to obtain the resistivity value, three parameters are measured: capacitance C, the Q-factor of the cell containing the sample under test, Q, and the frequency of the minimum Q-factor, f_{min}. The appropriate fit to the experimental data of C(f) and Q(f) dependencies give the resistivity value. The measurements can be performed using impedance analyzer.

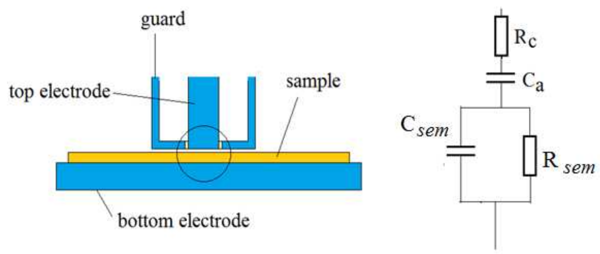

Fig. 5. *Capacitive measurement set-up for resistivity measurements of high resistivity semiconductors wafers and equivalent cuircut (after [4])*

The results of C(f) and Q(f) for highly resistive 2-inch substrate is presented in Fig. 6. As can be seen, no dispersion of C(f) and Q(f) could be identified. This means, that substates are purely dielectric with the resistivity value of at least 1x 10^{11} Ω cm

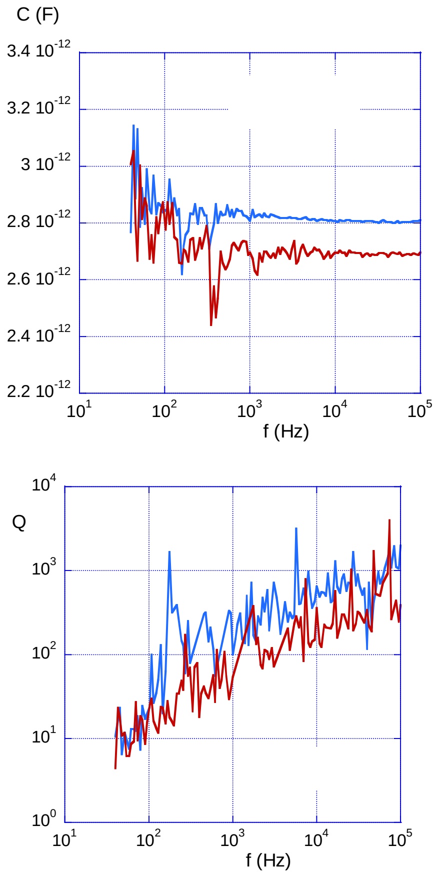

***Fig. 6**. Resistivity of two SI substrates from, measured by capacitance method in frequency domain. No dispersion in C(f) and Q(f) dependencies indicates the dielectric character of the substrates (resistivity at least 10^{11} Ω cm)*

Preliminary measurement of thermal conductivity (TC) by means of 3-omega method revealed 110±10 W/mK at room temperature. Such low TC value can be interpreted in terms of still too high impurity concentration and is a subject of further examination and improvement.

SUMMARY

The results of highly resistive 2-inch AMMONO-GaN substrates of reduced impurity concentration (concentration of donors and compensating acceptors at the level of 10^{18} cm^{-3}) and resistivity of at least 10^{11} Ω cm and outstanding crystallographic properties are presented. Measured resistivity is high enough to enable good electrical isolation of horizontal transport of two dimensional electron gas (2DEG) in HEMT transistors grown on such a substrate, while cleaner substrates minimize the diffusion of impurities into the quantum structures. Although thermal conductivity needs to be improved (TC=110±10 W/mK), the transistor performance may benefit of outstanding structural properties, which was documented by narrow rocking curve (FWHM=20 arcsec), large curvature radius (20-200m) and very low dislocation density (2x10^4 cm^{-2}). The substrates were polished to epi-ready standard (RMS-0.1-0.2 nm). The fabrication of 2-inch semi-insulating ammonothermal GaN substrates, which can be alternative to HVPE ones, is possible. Consequently, this can be a next step towards an efficient production of high-power, high-frequency devices based on GaN homoepitaxy.

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REFERENCES

[1] U. Mishra et al. , Proceedings of IEEE, **90**, 1022 (2002).

[2] R. Dwilinski, R. Doradzinski, J. Garczynski, L.P. Sierzputowski, A. Puchalski, Y. Kanbara, K. Yagi, H. Minakuchi, H. Hayashi, J. Crystal Growth **310**, 3911 (2008).

[3] R. Dwilinski, R. Doradzinski, L.P. Sierzputowski, R. Kucharski, M. Zając, Eletronika **53**, 11 (2012).

[4] J. Krupka, Meas. Sci. Technol. **24** 062001 (2013).