Extended Abstracts of the 1999 International Conference on Solid State Devices and Materials, Tokyo, 1999, pp. 58-59

Invited

Application of Pressure Grown GaN Substrates to Epitaxy

S. Porowski

High Pressure Research Center Polish Academy of Sciences,
ul. Sokołowska 29/37, Warsaw, Poland
phone: +48 22 632 50 10, fax: +48 22 632 48 12, e-mail: sylvek@unipress.waw.pl.

1. Introduction

Due to thermodynamical properties of GaN [1,2], the bulk crystallization of this compound is very complicated. In this paper, it is shown that the crystallization from solutions under high pressure of N_2 allows to grow GaN single crystals of quality and size suitable for epitaxy and device processing. Since the crystals are of very high structural perfection, they can be very useful for understanding the role of defects in physical processes occurring in devices based on standard heteroepitaxial structures.

2. Crystal Growth

High Nitrogen Pressure Solution growth (HPSG) of GaN is based on the three phase system of solid GaN and its constituents. The pressure of N_2 in the range of 1-2 GPa is used to increase the free energy of the constituents (mainly N_2) in relation to the crystal. This leads to the significant extension of GaN stability range. The application of 2 GPa N_2 pressure allows to approach 2000K. At this temperature, nitrogen can be dissolved in liquid gallium at the concentration of 1at.%. Dissolution of nitrogen in liquid gallium is preceded by dissociative chemisorption of N_2 with a potential barrier of about 4.8eV, as calculated by Krukowski et al. [3]. Beside the solutions in pure gallium, the solutions in Ga alloyed with Mg at concentrations of about 0.5 at.% are also used.

The supersaturations are created by the application of temperature gradient to achieve continuous transport of nitrogen from the hot to the cold zone of the crucible. The maximum rates of stable growth into directions (10-10) perpendicular to c-axis are ≤0.1mm/h, so centimeter size crystals are obtained in 100 - 200 hours processes.

The crystals are hexagonal platelets with thickness of 0.1 - 0.2 mm. Such shape indicates large anisotropy of the growth at the applied conditions. When Mg is added to the solutions, the crystals do not change their macroscopic form. The crystals doped with Mg during growth are perfectly colorless whereas the crystals grown without an intentional doping are slightly yellowish (Fig.1).

a b

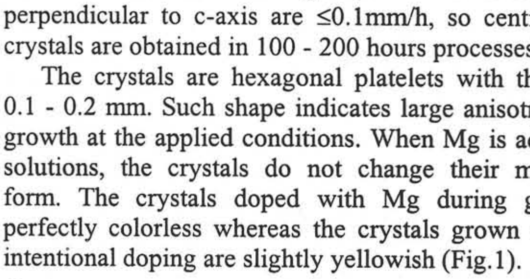

Fig.1 GaN crystals grown by HNPS method: a- without doping; b- Mg-doped, distance between grid lines is 1 mm.

3 Physical properties of GaN crystals

As it is summarized in Table 1, the crystals grown from solutions in pure Ga, without an intentional doping, are highly conductive whereas the growth from solutions in Ga alloyed with Mg results in highly resistive crystals.

Table 1 Electrical properties of GaN crystals

crystal	conductivity type	ρ, Ωcm, 300K	n ,cm^{-3}
GaN	metallic	$10^{-3}10^{-2}$	3-6 x 10^{19}
GaN : Mg	hopping	10^4-10^6	----

The main residual impurity detected in the crystals by SIMS is oxygen. The most probable native defects in highly n-type GaN, are Ga-vacancies (V_{Ga}^{3-})[4,5]. Their presence at concentrations of 10^{18} cm^{-3} , in the n-type pressure grown GaN crystals, has been detected by positron annihilation experiments [6]. In the Mg-doped crystals Ga-vacancies have not been found.

The increase of electrical resistance in GaN:Mg crystals is related to drastic decrease of free electron concentration. The temperature dependence of resistivity for these samples at low temperatures up to about 250K, suggests hopping type of conductivity [7]. At higher temperatures the conductivity starts to be governed by the activation process leading to the creation of free holes in the valence band.

Also the optical absorption data [7] indicate that the free carrier concentration in the Mg-doped GaN is very low. The free carrier absorption which dominates the low energy part of the spectra for the undoped GaN disappears for crystals grown from Mg containing solutions. For these crystals, the absorption coefficients for energies below the fundamental absorption edge are as low as 1-10 cm^{-1} .

The GaN substrate crystals grown by HPSG method are of high structural quality as determined by X-ray diffraction (XRD) [8], transmission electron microscopy (TEM) [9,10] and defect selective etching (etch pit density - 1-100 cm^{-2}) [11]. The X-ray rocking curves for symmetrical reflection are as narrow as 18-25 arcsec. for almost all Mg-doped crystals and for best crystals grown without doping. For some of the conductive crystals the rocking curves splits onto few peaks indicating low angle (about 1 arcmin.) grain boundaries. The rocking curves for in-plane reflections are always below 25 arcsec. what indicates that there is no twist mosaicity in all investigated crystals.

A number of GaN crystals have been studied by TEM. In most observations the crystals were completely free of dislocations.

4 Surface preparation

To obtain epi-ready surfaces of GaN substrates the polishing and etching are necessary. The mechanical polishing with diamond micropowders leads to the formation of highly damaged surfaces with scratches of 200 Å in depth. The thickness of the damaged layer under such surfaces is usually 2000-2500Å (RBS measurements [12]).

The $(000\underline{1})_N$ surface of the bulk GaN crystals can be etched in aqueous solutions (10N - 1N) of KOH and NaOH [13]. The free etching of this surface is strongly anisotropic and results in the formation of numerous stable pyramids 100 - 200nm in height.

The same solutions are used for mechano-chemical polishing of the $(000\underline{1})_N$ GaN surface [13] giving atomically flat. The RBS [12] and TEM [9] measurements indicate that the polishing removes the subsurface damage.

For Ga-polarity surfaces, the Reactive Ion Etching are used for removing the subsurface damage. Some roughness remaining after the RIE treatment is usually removed at the first stages of epitaxial growth.

5 Homoepitaxy

Epitaxial growth of GaN layers and GaN-based structures was tried on both polar surfaces of pressure grown GaN crystals, by MOCVD [i.e14,15] as well as by MBE with plasma [16] and NH_3 [17,18] nitrogen sources.

The growth by propagation of monoatomic steps has been achieved by both methods on both polar surfaces. Such a sequence of atomic steps usually covers whole surface of GaN substrate. However for the layers grown by MOCVD on $(000\underline{1})_N$ oriented substrates the hexagonal growth hillocks with the inversion domains inside [11] are often observed. This can be removed by proper surface preparation.

It was shown that the active surface of GaN is more sensitive to contaminations which often results in enhanced incorporation of impurities during epitaxy in comparison to the inert surface of the GaN substrates. Probably due to this reason the best PL spectra were obtained for layers deposited on the inert, Ga-side of GaN substrates by both MOCVD [14,15] (Fig.2) and MBE [18].

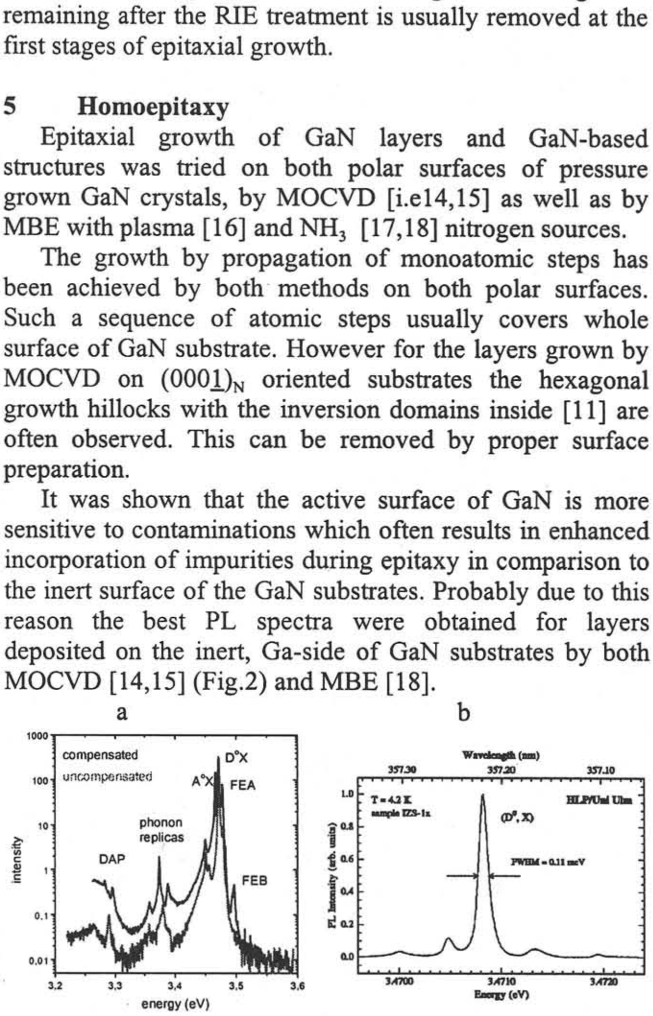

Fig.2 PL spectra of MOCVD GaN homoepitaxial layers a-compensated grown at University of Ulm [15], uncompensated - CRHEA, Valbonne [14], b - University of Ulm

The mechanisms of nucleation and growth by MBE on the N-polar surface of GaN is strongly dependent on temperature and III/V ratio. At the optimized conditions dislocation free layers and MQWs can be grown by 2D mechanism [16] - Fig. 3a. Too low temperature leads to the island growth. Due to the high structural quality of the substrate the coalescence of the islands is often perfect (without dislocations) - Fig. 3b.

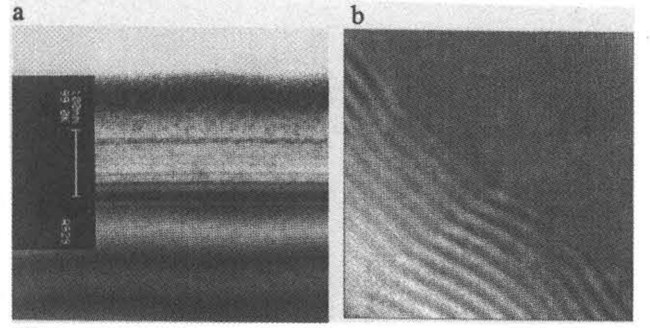

Fig.3 TEM images of the multilayer GaN/ $Al_{0.1}Ga_{0.9}N$ structures grown by plasma source MBE [16]: a - growth temperature - 780°C, b - growth temperature - 650°C

These experiments showed that even 150 nm thick $Al_{0.1}Ga_{0.9}N$ can be grown without relaxation. For thicker layers the relaxation be rearrangement of surface morphology (undulation) was observed.

6 Device processing

The pressure grown GaN crystals can be subjected to all the procedures like photolithography, cleaving or cutting, necessary for making optoelectronic devices.

References

[1] J. Karpinski., J. Jun and S. Porowski , *J.Cryst. Growth*, 66, 1, (1984)

[2] I. Grzegory, J. Jun, M. Bockowski, St. Krukowski, M. Wroblewski, B. Lucznik and S. Porowski, J. Phys. Chem. Solids **56**, 639 (1995)

[3] S. Krukowski S, Z. Romanowski ,I. Grzegory and S. Porowski, Journal of Crystal Growth vol.189-190, pp.159-62, (1998)

[4] P. Boguslawski, E. Briggs and J. Bernholz, *Phys. Rev.* B51, 17255, (1995)

[5] J. Neugebauer and C. G. Van de Walle, *Phys. Rev.* B50, 8067, (1994)

[6] K. Saarinen, T. Laine, S. Kuisma, P. Hautojarvi, L. Dobrzyński, J. M. Baranowski, K. Pakuła, R. Stępniewski, M. Wojdak, A. Wysmołek, T. Suski, M. Leszczyński, I. Grzegory and S. Porowski, Phys. Rev Lett. 79, 3030, (1997)

[7] S. Porowski, M. Bockowski, B .Lucznik, I. Grzegory, M. Wroblewski, H. Teisseyre, M. Leszczynski, E. Litwin-Staszewska, T .Suski, P. Trautman, K. Pakula and J.M. Baranowski, Acta Phys. Pol.A, vol.92, no5, (1997), 958-962

[8] M. Leszczynski, I. Grzegory, H. Teisseyre, T. Suski, M. Bockowski, J. Jun, J. M. Baranowski, S. Porowski and J. Domagala, J. of Cryst. Growth 169, 1996, 235-242.

[9] Z. Liliental-Weber, private communication

[10] M. Albrecht, private communnication

[11] J. Weyher et al. to be published

[12] M. Conway, J. S. Williams and C. Jagadish, private com.

[13] J.L. Weyher, S. Müller, I. Grzegory and S. Porowski, J. Cryst. Growth 182, (1997), 17-22

[14] M. Leszczynski, B. Beaumont, E. Frayssinet, W. Knap, P. Prystawko, T. Suski, I. Grzegory and S. Porowski, Appl. Phys. Lett. Vol.75, n.9,p.1085

[15] C. Kirchner, V. Schwegler, F. Eberhard, M. Kamp., K.J. Ebeling, F. Kornitzer, T. Ebner, K, Thonke, R. Sauer, P. Prystawko, M. Leszczyński, I. Grzegory and S. Porowski, Appl. Phys. Lett. Vol.75, n.9, p. 1098

[16] C.T. Foxon, Proceedings of MRS Fall Meeting, Boston 1998

[17] R. Held, G. Nowak, B. E. Ishaug, S. M. Seutter, A. Parkhomovsky, A. M. Dabiran, P. I. Cohen, I. Grzegory and S. Porowski, J. Appl. Phys. Vol.85, no11, p.7679, 1999.

[18] J. Massies et al., to be published