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Influence of Dopants on Defect Formation in GaN

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Influence of p-dopants (Mg and Be) on the structure of GaN has been studied using Transmission Electron Microscopy (TEM). Bulk GaN:Mg and GaN:Be crystals grown by a high pressure and high temperature process and GaN:Mg grown by metal-organic chemical-vapor deposition (MOCVD) have been studied. Structural dependence on growth polarity was observed in the bulk crystals. Spontaneous ordering in bulk GaN:Mg on c-plane (formation of Mg-rich planar defects with characteristics of inversion domains) was observed for growth in the N to Ga polar direction (N polarity). On the opposite site of the crystal (growth in the Ga to N polar direction) Mg-rich pyramidal defects empty inside (pinholes) were observed. Both these defects were also observed in MOCVD grown crystals. Pyramidal defects were also observed in the bulk GaN:Be crystals.

Introduction

GaN can easily be grown with n-conductivity but obtaining p-doping is rather difficult. Only recently p-doping was also obtained by Be doping [1]. Mg is most commonly used as the p-dopant in GaN; however, higher hole concentrations can only be obtained after thermal annealing [2] in order to dissociate Mg-H complexes. Material made using this process has been used to fabricate light emitting diodes (LEDs) [3] and lasers [4]. Despite this success, many aspects of Mg-doping in GaN are still not fully understood. Transmission electron microscopy (TEM) studies show formation of different types of Mg-rich defects in many bulk crystals. The type of defects formed depends strongly on the growth polarity. In the bulk GaN:Mg platelet crystals, planar defects distributed in equal distances (20 unit cells of GaN) leading to superlattice reflections in the diffraction pattern can be observed [5-7] for growth with N-polarity. Similar defects are also formed in layers grown by metal-organic chemical–vapor deposition (MOCVD) with Mg delta doping [6-7]. For majority of platelet crystals grown with Ga polarity, formation of pyramidal defects empty inside but rich in Mg on their walls was observed. These pyramidal defects are also typical for all MOCVD-grown crystals, and their high concentration can be observed in all crystals for a wide range of Mg concentration.

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Bulk GaN:Be crystals are somehow similar to GaN:Mg. As-grown surface is rough for growth with N-polarity. However, spontaneous ordering was not observed. However, for growth with Ga polarity, pyramidal defects are also observed in some crystals.

Experimental

Different types of GaN crystals doped by Mg and some with Be have been studied using plan-view and cross-sectioned samples. Bulk crystals were grown by the High Nitrogen Pressure Method [8] from a solution of liquid gallium containing 0.1 - 0.5 at.% Mg [9]. Similar procedure was applied to GaN:Be crystals. Two types of samples were grown using MOCVD where Mg was added either continuously during the growth or by the delta doping method (one monolayer at each 100Å of GaN). The details of this growth have been described earlier [6-7]. Following the growth, the temperature was lowered to 850°C, the ambient was switched to nitrogen only, and a 10 minute *in-situ* anneal was performed to dissociate the Mg-H complexes and activate the Mg atoms [10]. The same growth temperature and post annealing was applied to the crystals for which Mg was added continuously during growth. All GaN:Mg and the GaN:Be crystals have been studied using TEM on plan-view and cross-section samples, transparent for electrons, prepared by standard methods using Topcon 002B and JEOL ARM with the accelerating voltages of 200 and 800 kV, respectively.

Results

A strong dependence of structure on crystal growth polarity was observed in bulk platelet crystals. For the crystal side grown with N polarity (N to Ga direction) many crystals were free of defects, but Mg-rich planar defects were observed in some crystals, despite the fact that Mg concentrations determined by SIMS remain practically unchanged. These defects
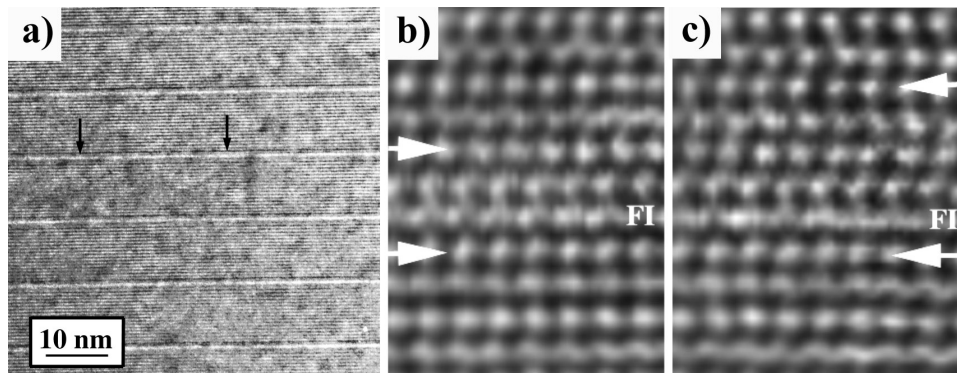

Fig.1: (a) TEM micrograph showing equi-distant arrangement of planar defects (inversion domain-ID) formed in bulk GaN crystal grown with N-polarity. Arrows indicate areas from which higher magnification micrographs are shown in (b) and (c), respectively. The white arrows in (b) and (c) indicate the position of perfect GaN matrix on both side of the planar defect. FI is a flat interface of the inversion boundary which remains on the same c-plane, but the upper interface, called corrugated interface (CI) is changing from place to place.

can be perfectly ordered for several micrometers from the sample surface. They can form a perfect array of planar defects separated from each other by 20 unit cells of GaN [5-7] (Fig. 1a). Perfect ordering leads to super-lattice spots dividing the (0001) lattice distance into 20 equal parts (not shown here). The following TEM results, e.g. presence of split (0001) reflection, reverse contrast for multi-beam dark-field (0001) and (000-1) reflections, symmetrical contrast in dark field (top and bottom surface of TEM foil) indicate that these planar defects are inversion domains [5-7] formed on c-planes with a very narrow width along the c-axis. In addition, it was observed that pairs of inversion boundaries in one domain are separated by not more than 1- 3 unit cells. One of the domain boundaries called the flat interface (FI) shown in Figs (1b and c) always remains on the same plane. The upper boundary, called the corrugated interface, changes its position, so that the domain wall thickness is changing from 3/2c to 5/2c as shown by high resolution images taken in two areas from the same defects (Figs. 1b and c). The distribution of these inversion domains is shown graphically on Fig. 2. Local change of thickness within one domain gives additional evidence that the observed planar defects are not stacking faults. EDX studies gave evidence of Mg enhancement within the domains [5]. This perfect ordering was not observed in all crystals studied. In some crystals this perfect ordering was interrupted by larger areas of hexagonal GaN or this ordering can be interrupted by stacking fault.
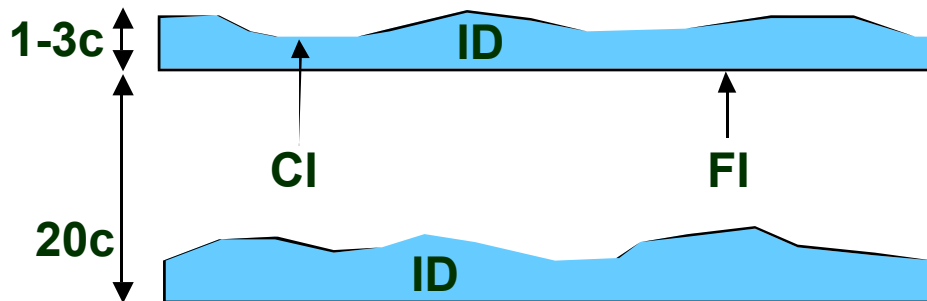

Figure 2: Schematic showing distribution of inversion domains (ID) in GaN grown with N-polarity. The thickness of particular domains is changing locally but distance between equivalent domains remains 20 c (unit cells).

The opposite side of the bulk crystals (grown with Ga-polarity) had a completely different defect structure as shown in Fig. 3 (a). They appear in [11-20] cross-section TEM micrographs as triangular features with a base on the (0001) c-plane and six side facets inclined 45° to the basal plane. The dimension of the largest defects varies. The longest base length of these defects are in the range 100 nm and the smallest about 3-5 nm. The density of these defects is in the range 2.5×10^9 cm^{-2}. All these triangles were oriented in a direction with the base closest and parallel to the sample surface with Ga-polarity, e.g. from the triangle tip to the base, the long bond direction along the c-axis is from Ga to N. Study of these defects in plan-view configuration prove that these defects are empty inside (Fig. 3b). EDX studies showed that Mg is segregated on the base and side-walls of these defects. High resolution TEM images from the defect base show the formation of planar defect.
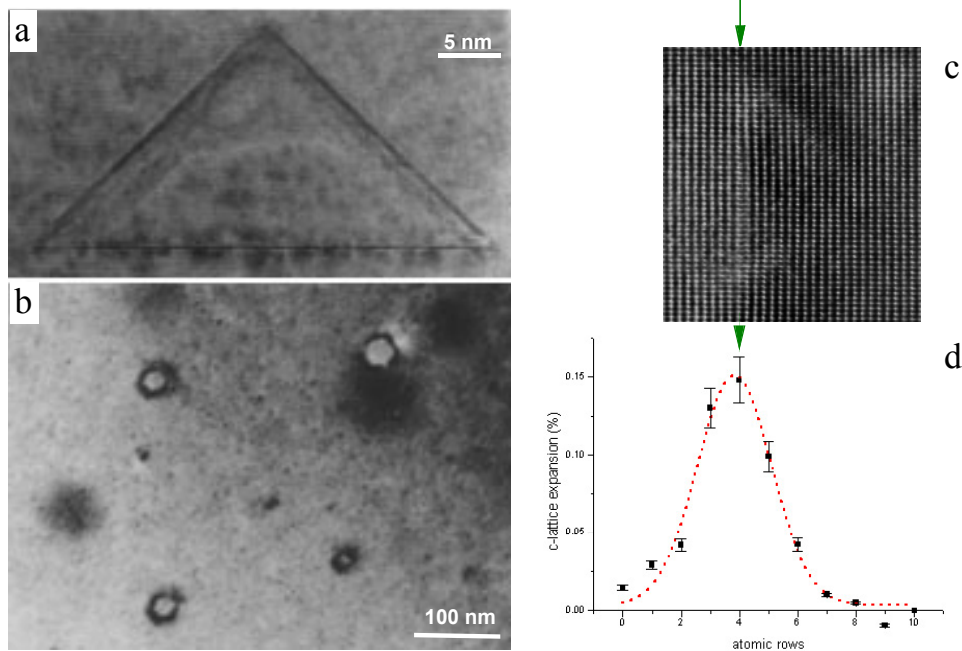
Fig. 3. (a) TEM cross-section micrographs showing defects formed in platelet GaN:Mg bulk crystals on the side grown with Ga polarity observed in cross-section, (b) the same defects observed in plan-view configuration; (c) high resolution micrograph observed in MOCVD grown crystals showing expansion of the interplanar distances in the defect base; (d) measured lattice expansion in the defect base.

GaN:Mg layers grown by MOCVD

Since the majority of layers applied in devices are grown by MOCVD it was also interesting to observe the structure of p-doped layers to learn why p-doping is so difficult [2]. Two types of crystals have been studied: one where Mg was added as delta doping, to study if addition of a monolayer of Mg at equal distances will lead to the ordering observed in bulk crystals and the second where Mg was added continuously, as used for growth in devices.

Cross-section TEM studies of Mg-delta doped samples show both types of defects observed for the two opposite growth polarities in bulk GaN:Mg, e.g. planar defects observed earlier for N growth polarity and pyramidal defects observed in the bulk GaN:Mg for growth with Ga polarity [5-7]. In a crystal with Mg-delta doping, planar defects were formed followed by a high density of pyramidal defects. In this crystal a layer about 100 nm thick with planar defects (Fig. 4a), like those observed in bulk crystals grown with N-polarity, was observed at about 150 nm distance from the buffer layer. This suggest that some accumulation of Mg on the surface is needed for the first Mg-rich planar defect to appear. Further growth resulted in a random distribution of pyramidal defects with a density of $\sim 10^{10}$ cm^{-2}. High -resolution TEM images from the defect base show an expansion of the

interplanar distance (Fig. 3c): 14% expansion was measured (Fig. 3d). This value was compared to the expansion expected if Mg, MgO, MgO_2, or predicted theoretically Mg_3N_2 phase would be formed on the defect base. The best agreement was obtained for Mg accumulating on the c planes in the base of these defects (Table 1).

Table 1: Calculated expansion of interplanar distances in the pyramidal defect base for different materials

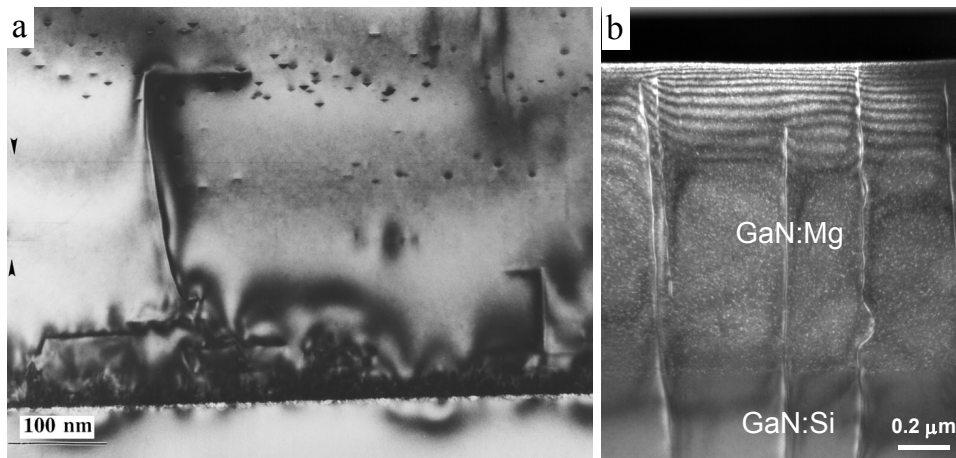|	GaN	
	c/2 = 2.585 Å	a = 3.18 Å
MgO a/2 = 2.585 Å	18%	
MgO_2 a/2 = 2.422 Å	6%	
Mg a = 2.95 Å	14%	7%
Mg_3N_2 a/4 = 2.45 Å	4%	

Fig. 4 (a) Cross-section TEM micrographs showing a layer with delta doping grown with GaN buffer layer on sapphire. The area between the arrows shows planar defects similar to these observed in bulk platelet crystals grown with N-polarity. These planar defects delay to appear compared to the expected location of the first monolayers of Mg. Above the top arrow, Mg monolayers were not found, but pyramidal defects (same as in bulk crystals grown with Ga polarity) in high density were observed. Some of these pyramidal defects started to appear simultaneously with the planar defects.(b) A layer of GaN:Mg with continuous Mg doping. Note high density of pyramidal defects (white dots).

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   SIMS analysis in the layers with Mg delta doping indicated that Mg concentration was steadily increasing and it reached the level of 4×10^{19} cm^{-3} in the area with planar defects [7]. In the area where the hollow defects (rectangular and triangular) were formed Mg concentration dropped to 2×10^{19} atoms/cm^3 and stayed almost constant with a slow increase to reach a concentration of 4×10^{19} at the sample surface[7].
   In the samples where Mg was added continuously (with comparable Mg concentration to that in the previous samples), no planar defects were observed but a high density of pyramidal defects was present (Fig. 4b). These pyramids are also empty inside but their size was much smaller compared to these observed in bulk platelets (8 nm in the base). At the base of these defects stacking faults were not formed as in the larger pyramids observed in the bulk samples. However, the expansion of the lattice parameter of about 14% was observed in two basal parallel layers (Fig. 3c and d). The expansion agrees well with what would be expected if Ga atoms were substituted by Mg.

   Table 2. SIMS analysis of bulk platelets for growth with N- and Ga-polarity where either ordering (ord) or pyramidal defects (def) were observed and defect free samples (no ord. and no def) compared to MOCVD samples grown with Mg delta (δ) doping and continuous (c) Mg doping. Concentralion for particular elements (cm^{-3}).

Sample	Mg	O	C	Si
A N-ord Ga-def	2e20-6e19 6e19	2.5e19	1.5e17	4e16
B N-par.ord Ga-no def	5e19	3e19	5e19	1e16-1e17
C N-no ord. Ga-def	4-7e19	2e19	3e17	1-3e17
D N-no ord. Ga-no def.	4-6e19	7e19	1.5e18	1-2e19
MOCVD-δ ord.+def.	1.5-3e19	5e16	5e16	----
MOCVD-c def	3e19	5e16	5e16	

Discussion of Mg results
   TEM studies of bulk crystals grown under high pressure and high temperature doped with Mg and those grown by MOCVD show formation of structural defects for a wide range of Mg concentration. This would explain (at least to some extend) why it is so difficult to obtain high hole concentration despite nominal higher Mg concentration in the crystal. Since p-conductivity was not obtained in bulk crystals, but GaN:Mg samples became semi-insulating, some compensation of oxygen presence in these samples took place. Ordering of planar defects observed in GaN:Mg formed for growth with N-polarity

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appears to be similar to the polytypoids formed in AlN rich in oxygen [11]. But it appears that similar defects were formed in MOCVD grown samples, where oxygen concentration was three orders of magnitude lower. Therefore, it is believed that mainly Mg is responsible for the formation of these defects. Our studies of bulk samples from two opposite sides, e.g. grown with N and Ga-polarity, do not indicate substantial difference in Mg incorporation for different growth polarity as predicted theoretically [12] and observed in MBE grown samples [13], where up to 30 times more Mg was incorporated in Ga-polarity, as determined by secondary ion mass spectrometry. The last authors [13] also indicated accumulation of Mg on the sample surface which would be consistent with our results.

GaN:Be bulk samples

TEM studies of Be-doped GaN platelet crystals show many similarities to the samples grown by the same method with Mg. However, ordering was not observed in these samples. For growth with N-polarity as-grown crystals appear to have rough surface (Fig. 5a) and the growth with Ga polarity results in smooth surface (Fig. 5b). Only three crystals have been studied. Two of them did not show any structural defects, but pyramidal defects have been observed in one of them Figs. (5c and d). The size of these pyramids appear much smaller in comparison to those observed in Mg doped platelet samples. The length of the base of these defects is in the range of 5-10 nm, similarly to the sizes observed in GaN:Mg grown by MOCVD. The density of these defects appears also lower in comparison to Mg doped crystals. These samples are also semi-insulating.
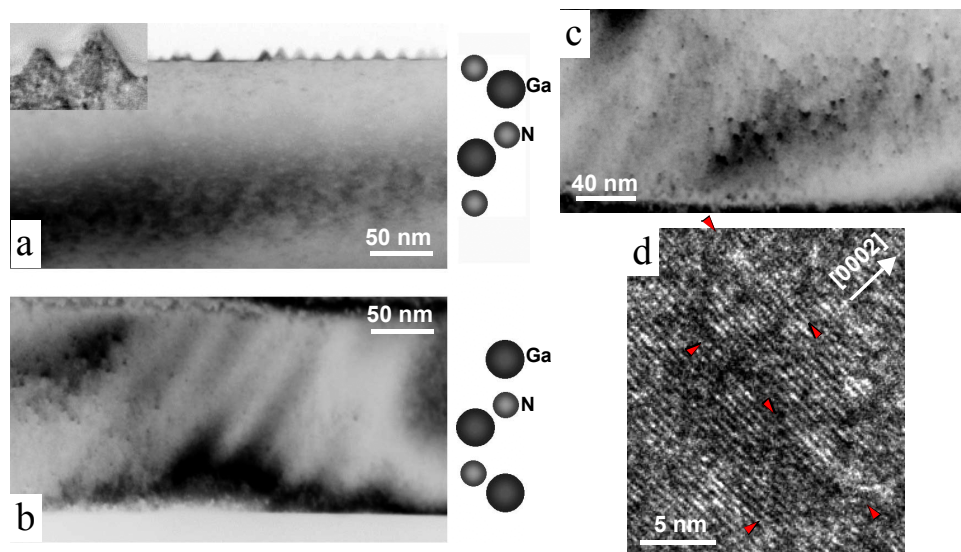

Fig. 5: (a) TEM micrograph of GaN:Be platelet with corrugated surface. (b) The same sample from the opposite side showing flat surface. (c) Part of another platelet crystal grown with Ga polarity with pyramidal defects (small dots). (d) High resolution image of two pyramids which corners were indicated by arrows.

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Summary

TEM studies of Mg-doped GaN crystals show formation of structural defects for a wide range of Mg concentration strongly influenced by crystal growth polarity. Similar defects are formed for bulk crystals grown under high hydrostatic pressure and for those grown by MOCVD. In some bulk crystals for the plate side grown with N-polarity equally distributed planar defects were observed (20 unit cells). Each defect appears to be an inversion domain with domain thickness about 1-3 unit cells along c-axis. No inversion in the GaN between these planar defects was observed.

Pyramidal defects, were observed for growth with Ga polarity, also due to Mg segregation. These defects were observed in the majority of bulk GaN samples and in all samples grown by MOCVD. When these pyramids are small, a 14% lattice expansion can be detected in the bases of the pyramids consistent with the substitution of Ga by Mg atoms.

The samples grown with Be doping show similarities with Mg- doped samples in respect to their surface roughness and formation of pyramidal defects in some crystals. Planar defects were not observed in these crystals. Semi-insulating properties were measured in the crystals doped with Mg and Be.

References

1. T.H. Myers, .A.J. Ptak, ; L. Wang, .N.C. Giles, . Proc. Int. Workshop on Nitride Semiconductors, Nagoya, Japan, 24-27 Sept. (2000).
2. H. Amano, M. Kito, K. Hiramatsu, and I. Akasaki, Inst. Phys. Conf. Ser. **106**, 725 (1989).
3. S. Nakamura, M. Senoh, and T. Mukai, Jpn. J. Appl. Phys. **31**, L1708 (1991).
4. S. Nakamura, Paper Plenary 1, presented at the 24th International Symposium on Compoud Semiconductors, San Diego CA, 8-11 September (1997).
5. Z. Liliental-Weber, M. Benamara, J. Washburn, I. Grzegory, and S. Porowski, Phys. Rev. Lett. **83**, 2370 (1999).
6. Z. Liliental-Weber, M. Benamara, W. Swider, J. Washburn, I. Grzegory, S. Porowski, D.J.H. Lambert, C.J. Eiting, and R.D. Dupuis, Appl. Phys. Lett. **75**, 4159 (1999).
7. Z. Liliental-Weber, M. Benamara, W. Swider, J. Washburn, I. Grzegory, S. Porowski, D.J.H. Lambert, C.J. Eiting, and R.D. Dupuis, Physica **B 273-274**, 124 (1999).
8. I. Grzegory , J. Jun, M. Bockowski, S. Krukowski, M. Wroblewski, B. Lucznik, and S. Porowski, J. Phys. Chem. Solids **56**, 639 (1995).
9. 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 Physica Polonica A **92**, 958 (1997).
10. C.J. Eiting, P.A. Grudowski, J.S. Park, D.J.H. Lambert, B.S. Shelton, and R.D. Dupuis, J. Electrochem. Soc. **144**, L219 (1997).
11. R.A. Youngman, A.D. Westwood, and M.R. McCartney, Mat. Res. Soc. Symp. Proc. 319, 45 (1994).
12. C. Bungaro, K. Rapcewicz, and J. Bernholc, Phys. Rev. **B59**, 9771 (1999).
13. A. J. Ptak and T. H. Myers, L. T. Romano, C. G. Van de Walle, and J. E.Northrup, Appl. Phys. Lett. 78, 285 (2001).