Application of XRD methods for the pilot studies of new functional materials for photonics

M. Dermeneva¹, D. Muravijova¹,², M. Mynbaeva², V. Bougrov¹, M. Yagovkina²

¹ ITMO University, Saint-Petersburg 197101, Russia
² Ioffe Institute, Saint-Petersburg 194021, Russia

Abstract. We report on the detailed study of the structural properties of the large-area GaN slabs grown by HVPE method over ceramic support with the use of X-ray analysis with powder diffraction technique. The impact of V/III ratio on the specifics of the crystal structure of the material was studied. It was shown, that depending of growth condition either texture along (00.2) axis, i.e., along c axis in polar GaN, or along (11.0) axis, i.e., normal to so-called m-plane GaN are formed.

1. Introduction

III-nitride group materials are employed in short-wavelength light-emitting diodes, lasers and optical detectors, as well as for high temperature, high power and high frequency semiconductor devices. Despite the fact that monocrystalline III-nitride compounds remain the most hot topic, the last decade has seen progressively developed polycrystalline nitride materials, which are easier and less expensive to fabricate. Among different group-III nitrides, GaN has shown great potential in the above applications, yet very little has been reported on polycrystalline GaN so far [1-6]. We have already reported on large-area crystalline gallium nitride slabs produced with hydride vapor-phase epitaxy (HVPE)-like deposition directly on a ceramic support, without using traditional substrates made of sapphire (Al₂O₃), silicon (Si) or silicon carbide (SiC). It was found that the obtained material was n-type semiconductor with optical, thermal, and mechanical properties close to those of single-crystalline GaN produced with traditional growth techniques [7]. At the same time, preliminary studies indicated that the nucleation process for our material strongly differed from that typical of HVPE of GaN layers on conventional substrates. In particular, for our material, a liquid phase formed at the initial stage of the growth process, and this resulted in self-oriented gallium nitride growth with an ordered block structure. In this work, we report on the detailed study of the structural properties of the large-area GaN slabs with the use of X-ray analysis with powder diffraction technique. This is the basic approach in the studies of polycrystalline materials, including textured ones, where «texture» (or preferred orientation) is termed for the samples whose grains are aligned in particular orientations. The preferred orientation has a dominant effect on the intensities of diffraction peaks in the XRD patterns. In this work, we used X-ray diffraction analysis for the study of the material of large-area GaN slabs, and in particular, the impact of V/III ratio during the growth on the specifics of the crystal structure of the material.
2. Experimental details
A set of samples with thicknesses 200–1500 μm was prepared. The samples were cut from GaN slabs which were grown under different conditions (different V/III ratio) and represented monolithic plates with a mechanically polished top surface (samples #1, 3 and 4). Parts of the samples adjacent to the ceramic substrate (back sides) were not polished, but chemically treated after the processing. Specimen #2 with thickness 200 μm was studied as-grown.

X-ray diffraction (XRD) analysis was performed with the use of Bruker D2 Phaser diffractometer (CuKα line was used with the wavelength 0.1540518 nm). The analysis of the diffraction patterns was carried out with DIFFRAC.EVA (Bruker Corp.) software using data from Powder Diffraction File ICCD PDF-2 release [JCPDS-International Centre for Diffraction Data (http://www.icdd.com)].

3. Results
Figure 1 shows optical images of 1500μm-thick samples. The images were obtained with an optical scanner in a transmitted-light mode. It can be seen that the samples are transparent and have a yellowish tinge. For the material grown under higher V/III ratio (shown in Fig. 1 (b)), one can note a peculiarity of the GaN growth mechanism at the stage of nucleation. In particular, nucleation islands are clearly visible at the back side of the plate in the transmitted light.

Figure 1. Images of two samples obtained in a transmitted-light mode: a, sample #3; b, sample #4. The area shown in the images is approx. 1 cm². Higher saturation of Ga (III) was used at the initial stage of HVPE process in the case of the sample shown in image b, where islands at the back side of the sample are visible.

Figures 2 and 3 show diffraction patterns from the investigated samples, which were obtained for both their sides. Black curves correspond to the top surface of the samples, red curves correspond to their back sides. By blue color lines with corresponding Miller indexes a diffractogramm, corresponded to the hexagonal GaN, are presented. Peaks corresponded to additional phase are marked by “Met” for metallic gallium and “Cub” for to the cubic phase of GaN. The «β» symbol shows the position of CuKβ peaks, which correspond to (00.2) and (11.0) reflexes. These patterns correspond to diffraction from polycrystalline material. In particular, diffraction patterns from all the samples show a set of diffraction maxima with various intensities in the range of angles from 20 to 100 degrees at the 2θ scale (for clarity, a smaller angle range is shown in both figures). Table 1 shows sizes of coherent-scattering regions (CSR), which were calculated both for the average size of the crystallites and for the preferred directions depending on the type of texture.

X-ray phase analysis allowed for unambiguous identification of all the maxima in the diffraction patterns of the top surface of sample #1. Comparison of experimental data with line diagrams acquired with X-ray phase analysis showed that the position of all peaks corresponded to the table data for hexagonal GaN (PDF file #01-073-7289). It is known that the most strong (10.1) maximum for polycrystalline non-textured GaN has 2θ of 36.8 degrees. At the same time, for this sample the strongest peak, whose intensity exceeded those of other peaks by almost two orders of magnitude, was observed at
57.7 degrees. Let us note that for this maximum, there is a corresponding CuKβ peak at the diffraction pattern. Such incompatibility of the intensity of the observed maximum with the table data can be explained by the presence of crystallites preferably oriented along (11.0) axis and their large dimension in this direction. As is shown in Table 1, for this sample the size of CSR along (11.0) axis constitutes 50 nm with averaged size of CSR calculated for all maxima being 35 nm. Diffraction pattern from the back side of sample #1 was almost identical to that from its top surface. The former also demonstrated similar, in terms of position and intensity, set of maxima, which corresponded to hexagonal GaN textured along (11.0) axis, with CSR size of ~120 nm. Weak maxima observed at 2θ of 33, 40 and 47 degrees may be related to metallic Ga (PDF file #00-005-0601) and cubic GaN (PDF file #00-052-0791).

![Figure 2. Diffraction patterns: (a), sample #1, (b), sample #2.](image)

![Figure 3. Diffraction patterns: (a), sample #3, (b), sample #4.](image)

**Table 1 Coherent-scattering regions in the studied samples**

| Sample # | Investigated area | Sample thickness, µm | SCR size, nm |
|----------|-------------------|----------------------|--------------|
|          |                   |                      | The average size of the crystallites | The size of crystallites along (00.2) axis | The size of crystallites along (11.0) axis |
| 1        | top surface       | 1000                 | 35           | -             | 50           |
|          | back side         |                      | 120          | -             | 120          |
| 2        | top surface       | 200                  | 80           | -             | 80           |
|          | back side         |                      | 70           | -             | 120          |
| 3        | top surface       | 1500                 | 45           | 45            | 54           |
|          | back side         |                      | 35           | 36            | 36           |
| 4        | top surface       | 1500                 | 50           | 100           | 63           |
|          | back side         |                      | 35           | 38            | 47           |

Diffraction pattern from the back side of sample #2 (which was thinner than sample #1) shows only maxima typical of hexagonal GaN with clearly expressed texture along (11.0) axis and CSR size of 70-120 nm. The pattern obtained from the top surface of this sample also agrees well with that typical of hexagonal GaN. The texture was expressed somewhat weaker, with CSR size being 80 nm. As follows from the data in figure 2(b), the main feature of this pattern is the presence of cubic GaN, which is expressed in extra maxima with high intensity at 2θ of 40, 85 and 97 degrees (PDF file #00-052-0791).

The results of X-ray diffraction analysis of samples ## 3 and 4 showed that these samples represented hexagonal GaN. The main difference between these samples related to the size of
crystallites (see table 1). The position of the most strong peak at $2\theta$ of 34 degrees indicates preferable orientation of the crystallites along (00.2) axis. At the same time, some texture along (11.0) axis is also present. This pattern is most clearly expressed for the top surface of sample #4, where the size of the crystallites along these two axes exceeds the average size of the crystallites: CSR along (00.2) axis is 100 nm, and along (11.0) axis, 63 nm, while the average CSR is only 50 nm. As a result of this, the strongest peaks at the diffraction pattern correspond to diffraction from (00.2) ($2\theta=34.56$), (11.0) ($2\theta=57.76$) and (00.4) ($2\theta=72.90$) planes. Note that for the first two maxima at the diffraction pattern the corresponding Cu K$_\beta$ peaks are also present.

Thus, X-ray diffraction and X-ray phase analysis of the studied samples showed that the material under study was in fact hexagonal GaN with a certain texture. Samples # 1 and #4 grown under higher III/V ratio with thickness larger than 1 mm, had texture along (11.0) axis or a mixed-type texture. These samples also contained some metallic Ga. Samples obtained at low III/V ratio (lower Ga saturation) had the majority of grains oriented along (00.2) axis (sample #3). All the samples demonstrated increase in texture grain size towards the surface. In the thin sample #2 that contained both hexagonal and cubic GaN phase the texture was pronounced to the least degree.

4. Discussion
It was mentioned in our previous work [7] that the nucleation process of the material under investigation strongly differed from that typical of HVPE of GaN on conventional substrates; specifically, the process considered in our work involved a liquid phase formed at the initial stage of the growth. From the one hand, this favors free detachment of GaN slabs from the surface of the ceramic support, but from the other hand, it affects the specifics of self-arranged orientation in the resulting textured crystal, as follows from the results of the present study. Thus, one may suggest that self-arranged orientation of texture structure reported here is favored by Ga/N ratio at the initial stage of nucleation of GaN. In the presence of excessive gallium, the preferred orientation is (11.0); texture (00.2) is formed under smaller Ga/N ratios. This is illustrated by the images in figure 1. There, one can clearly see the difference in morphology of back sides of samples #3 and #4. Figure 1(b) shows island-like morphology of the back side of sample #4, indicating that eventually excessive Ga droplet formation occurred. In this case, a mixed (11.0) and (00.2) orientation texture is formed. In contrast to this, sample #3 with a uniform (00.2) texture has a uniform planar back side.

The above made conclusion is supported by the existing knowledge on the kinetics of Ga adsorption on various types of substrates, as well as on the influence of Ga/N flux ratio on the growth mechanism, and thus, on the crystalline quality and chemical composition of GaN [8-11]. In particular, it was shown that under certain conditions, at high temperatures, Ga may adsorb layer-by-layer at the growth front up to continuous film, which may evolve into metallic Ga droplets. Spontaneous nucleation and growth of self-oriented GaN layers or textures on top of the molten gallium may occur if the gallium is exposed to nitrogen. For the case of GaN (00.1), the optimum growth conditions are related to the formation of just a metallic Ga bilayer at the growth front. In contrast to this, GaN (11.0) growth is provided by excesses of Ga adlayer (or droplets), which shifts the growth conditions towards Ga-rich ones.

Concerning the observation of cubic phase, we should note that in our previous work we performed the analysis of defect structure in gallium nitride crystals with the use of high-resolution transmission electron microscopy (HRTEM). These studies demonstrated that the GaN material with an ordered micro-block structure of hexagonal phase contained blocks with a different degree of mis-orientation, up to 7$^\circ$ at the earlier stage of the growth. The predominant types of defects observed in the structure of conjugated mis-oriented blocks were multiple stacking faults (SFs) in the (00.1) plane with displacement vector (00.1) 1/3[1–100], and it could be considered as a fragment of cubic-in-hexagonal structure. Such type of defect is known to be metastable, and is formed by phase transformation provided by interfacial mismatch strain relaxation in GaN lattice.
5. Conclusion

In conclusion, X-ray diffraction analysis, which allowed for large-area scanning, enabled us to study the structure of textured GaN samples as depending on the growth conditions. The impact of V/III ratio on the specifics of the crystal structure of the material was established. In particular, it was shown that under different values of Ga saturation (Ga rich condition), evolution of GaN structure resulted either in formation of texture along (00.2) axis, i.e., along c axis in polar GaN, or along (11.0) axis, i.e., normal to the so-called m-plane in GaN. The later observation seems to be quite important, since it is known that building GaN-based devices along the polar c-axis results in charge separation, spontaneous polarization, and degraded device performance. Building devices on the m-plane, a non-polar one, where there is no net polarization, radiative efficiencies should be higher, and no wavelength shift occurs, is much more preferable.

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