On the lattice parameters of GaN

V. Darakchieva[a] and B. Monemar
Department of Physics, Chemistry and Biology, Linköping University, S-581 83 Linköping, Sweden

A. Usui
R&D Division, Furukawa Co., Ltd., Tsukuba, Ibaraki 305-0865 Japan

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The lattice parameters of low-defect density, undoped bulk GaN fabricated by hydride vapor phase epitaxy (HVPE) on (0001) sapphire and subsequent substrate removal, are precisely determined using high-resolution x-ray diffraction. The obtained values, $c=5.18523$ Å and $a=3.18926$ Å, are compared with the lattice parameters of freestanding HVPE GaN from different sources and found to be representative for state-of-the-art undoped HVPE bulk GaN material. A comparison with bulk GaN fabricated by the high-pressure technique and homoepitaxial GaN is made, and significant differences in the lattice parameters are found. The observed differences are discussed and a possible explanation is suggested. © *2007 American Institute of Physics*.
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Knowledge of material lattice parameters is essential from both a physical point of view and for device engineering. This issue is presently of particular importance for III-nitride materials and related technology since the reported lattice parameters of GaN show unusual large fluctuations and it is difficult to determine the *intrinsic* unstrained values. The main obstacle has been the lack of a native substrate in the growth process and consequent difficulties to prepare strain-free material. Among several alternatives to fabricate bulk GaN crystals, the high-pressure (HP) growth from solution[1] and halide vapor phase epitaxy[2,3](HVPE) offer the most promising results for the moment. The lattice parameters of HP bulk GaN and homoepitaxial GaN have been extensively studied.[4,5] The GaN crystals grown by the high-pressure method exhibit a very low dislocation density (10^2-10^4 cm^{-2}) but typically show a high free-electron concentration $N_e>10^{19}$ cm^{-3} (related to high O incorporation).[5] Such a high free-electron concentration was theoretically predicted[6] and experimentally confirmed[4] to produce measurable changes in the GaN lattice parameters through the size effect and the deformation potential effect. Therefore, although being very close, the lattice parameters of HP bulk GaN still deviate somehow from the intrinsic strain-free values. On the other hand, lattice parameters of bulk GaN fabricated by HVPE and substrate removal, showing $N_e\leqslant 10^{17}$ cm^{-3}, have only been reported for samples with a limited thickness.[7] The reported lattice parameters of HVPE GaN substrates scatter slightly, and for some cases they may still be affected by bending, residual strain and measuring procedure.[7–9]

In this work, we report on a precise determination of the lattice parameters of 2-mm-thick bulk GaN fabricated by HVPE at Furukawa Co., Japan. The 15×10 mm^2 bulk sample was prepared using a facet-initiated lateral epitaxial overgrowth technique on (0001) sapphire and subsequent removal of the substrate.[3] The Ga face is as grown while the N face was chemically polished. Figure 1 shows a reciprocal space mapping (RSM) around the GaN 105 reciprocal lattice point from the Ga face of the bulk HVPE GaN [Fig. 1(a)] in comparison with the Ga face of a 300 μm HVPE freestanding GaN [Fig. 1(b)]. The latter was obtained by removing the layer from the (0001) sapphire substrate by laser lift-off. The two RSMs have the elliptical shape typical for III-nitrides with a mosaic structure. The RSM from the bulk HVPE GaN is considerably narrower in the ω direction compared to the freestanding layer, as a result of minimizing both curvature and dislocation density. An upper limit for the latter was estimated to be below 10^6 cm^{-2}. This high crystallographic perfection and low dislocation density is manifested in very narrow rocking curves (RCs) of symmetric and asymmetric peaks. For instance, the Ga face 006 and 205 RCs are about 22 arc sec (Table I). IR spectroscopic ellipsometry measurements on the bulk HVPE GaN reveals an $N_e<10^{17}$ cm^{-3}. Furthermore, low temperature (2 K) photoluminescence (PL) measurements reveal sharp dominant lines associated with the recombination of the *A* exciton bound to O and Si donors with full width at half maximum (FWHM) less than 0.3 meV. The latter evidences the low background donor concentration ($<5\times 10^{16}$ cm^{-3}) and confirms the high structural quality of the material. Such low-defect density material is therefore the prime choice for establishing the lattice parameters of bulk GaN fabricated by HVPE.

The *c* and *a* lattice parameters of GaN were determined from the symmetric 002, 004, and 006 and asymmetric 104, 105, 204, and 205 2θ-ω high-resolution x-ray diffraction (HRXRD) spectra. The symmetric and asymmetric scans were measured each at four and six azimuthal positions, respectively.[7] Details about the HRXRD equipment and alignment procedures can be found in Ref. 10. The lattice plane spacing d^e_{hkl} is derived from the Bragg angle θ_{hkl} for every reflection using Bragg's law and taking into account the refraction correction.[11] The lattice parameters *c* and *a* were obtained from the weighted nonlinear least-squares fit of $1/(d^e_{hkl})^2$ to the following equation:

$$\left(\frac{1}{d_{hkl}}\right)^2=\frac{4}{3}\left(\frac{h^2+k^2+hk}{a^2}\right)+\frac{l^2}{c^2}, \tag{1}$$

where d_{hkl} is the lattice spacings of a hexagonal crystal. The error Δd_{hkl},

[a]Author to whom correspondence should be addressed; Fax: +46 13 142337; electronic mail: vanya@ifm.liu.se

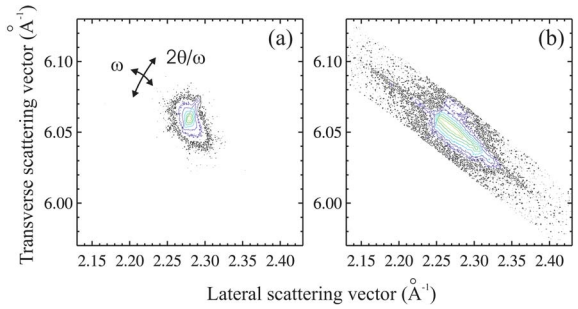

FIG. 1. (Color online) Reciprocal space maps around the GaN 105 reciprocal lattice point of (a) the 2-mm-thick HVPE bulk GaN and (b) 300-μm-thick HVPE GaN freestanding separated by laser lift-off from the substrate. The RSMs are normalized to the maximum intensity and the same seven contour levels (from 0.0001 to 1) equidistant in log scale are used in (a) and (b).

$$(\Delta d_{hkl})^2 = \left(\frac{\cos(\theta)\lambda\Delta\ \theta)}{2\ \sin^2(\theta)}\right)^2 + \left(\frac{\Delta\lambda}{2\ \sin(\theta)}\right)^2, \qquad (2)$$

is propagated to obtain the error of $1/d_{hkl}^2$, which is used to weigh the contribution of each reflection to the fit. In Eq. (2), λ is the x-ray radiation wavelength, θ_{hkl} is the angular position of the respective symmetric or asymmetric peak, $\Delta\theta$ is 15(6) arc sec, and $\Delta\lambda$ is 3.7×10^{-4} (3×10^{-4}) depending on the optics used.

The values of the lattice parameters and their errors for the Ga and N faces of the bulk HVPE GaN sample are summarized in Table I together with the FWHM of representative symmetric (006) and asymmetric (205) RCs. The lattice parameters of the two faces are very close to each other, with the c lattice parameter of the N face slightly larger, and the a lattice parameter slightly smaller than the respective counterparts of the Ga face. These subtle differences are, however, statistically significant and may be explained by polishing-induced changes in the lattice parameters. This speculation is supported by the larger RC widths of both symmetric and asymmetric peaks for the N face compared to the Ga face (Table I), which may be attributed to polish-induced damage.

Our results about the lattice parameters are plotted in Fig. 2 together with the lattice parameters of HVPE freestanding GaN material,[7,8] HP bulk GaN,[4,5] homoepitaxial GaN layer grown on HP bulk GaN,[4,6] and GaN powder.[12] Our lattice parameters are consistent with the previously published results for freestanding material fabricated by HVPE. It is seen that the lattice parameters of all HVPE samples form a distinct group (marked by a rectangular box in Fig. 2), well separated from the lattice parameters of the HP bulk and homoepitaxial GaN. The lattice parameters of GaN powder[12] also belong to this group. The slight differences between the lattice parameters of the HVPE samples may be due to the different nucleation schemes or thicknesses.[7]

Another reason for the observed fluctuations in the lattice parameters of the HVPE GaN (Fig. 2) may be related to the measuring procedure involved. The lattice parameters of the 2 mm bulk GaN reported in this work (Table I) are determined from a large number of reflections and sample positions ensuring high precision, much better than previously reported. It is important also to weigh the contribution of each reflection when fitting for the lattice parameters, as described above, since the difference between the relative precision of the interplanar spacings ($\Delta d/d$) may be as large as 32% depending on the reflections used. Note that the small errors of the lattice parameters of the 2-mm-thick bulk GaN (Table I) also reflect high in-depth and in-plane homogeneity. In view of the above discussion and the superior material properties of the 2 mm bulk GaN sample studied in this work, we may then infer that its lattice parameters, c =5.18523 Å and a=3.18926 Å, may be taken as representative for state-of-the-art (undoped) bulk GaN fabricated by HVPE.

TABLE I. Lattice parameters c and a and GaN 006 and 205 rocking curve FWHM (in arc sec) of the Ga and N faces of the HVPE bulk GaN.

	c(Å)	a(Å)	$FWHM_{006}$	$FWHM_{205}$
Ga face	5.185 23±0.000 02	3.189 26±0.000 04	21.5	21.6
N face	5.185 28±0.000 02	3.189 15±0.000 03	37.6	37.9

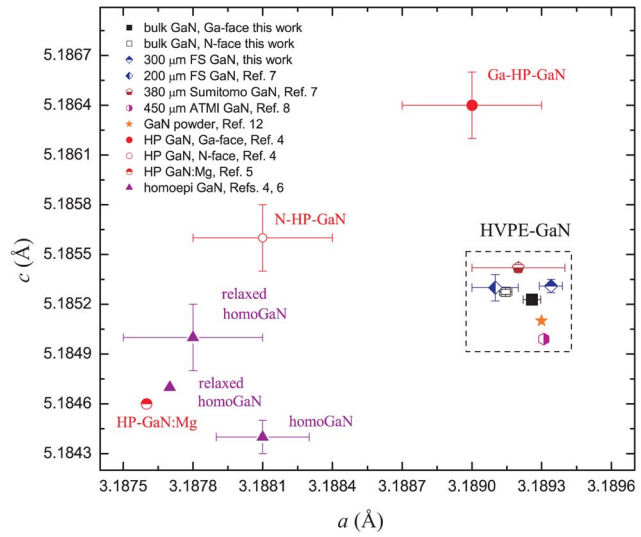

FIG. 2. (Color online) Lattice parameters a and c for bulk and freestanding GaN fabricated by HVPE, HP bulk GaN, and homoepitaxial GaN layer.

The two types of HP bulk material: unintentionally doped with a free-electron concentration $\sim5\times10^{19}$, HP GaN, and high-resistivity GaN grown from Ga:Mg solution, HP GaN:Mg, exhibit lattice parameters that significantly differ from those of the HVPE bulk GaN (Fig. 2). Both c and a lattice parameters of the HP GaN are larger compared to those of the HP GaN:Mg. This difference may be attributed to the expansion of the HP-GaN lattice related to the high free-electron concentration due to O incorporation in the material during growth. On the other hand, the deformation potential effect cannot be evoked to explain the difference between the lattice parameters of HP and HVPE GaN since N_e in the latter is well below 10^{17} cm^{-3}. Surprisingly, the a lattice parameter of the HVPE bulk GaN appears to be larger than that of the highly conductive HP GaN by 0.00026 Å (Fig. 2). The size effect related to O impurities and native defects in the HP GaN, such as Ga vacancies and their complexes with O_N could not explain the observed difference, since all are expected to expand the lattice. In this respect, we note that the Ga vacancies are found to be abundant in the HP GaN ($\sim10^{18}$ cm^{-3}),[13] while their concentration was reported to be two orders of magnitude less in HVPE GaN with a free-electron concentration below 10^{17} cm^{-3}.[14] The situation becomes even more puzzling when we consider the differences in the lattice parameters of HVPE GaN and

highly resistive HP GaN:Mg: the HVPE bulk GaN has *a* and *c* lattice parameters that are larger compared to the HP GaN:Mg (Fig. 2). However, the HP GaN:Mg contains high concentrations of Mg and O (both typically $\sim 10^{20}$ cm^{-3}), which should expand the lattice through the size effect if incorporated as isolated impurities.[6] Evaluation of the size effect for the HP GaN:Mg is further complicated by the existence of three-dimensional pyramidal defects, suggested to originate from Mg clusters,[15] and a possible presence of N vacancies and complexes, MgO, Mg–O–N clusters with unknown effect on the lattice parameters.[6] We also note that the size effect related to the Si impurity (typical for HVPE GaN) is negative.[6] We may then suggest that the presence of point defects alone cannot provide a plausible explanation for the observed differences between the lattice parameters of bulk GaN grown by HP and HVPE. Similarly, the deformation potential and size effects related to common impurities cannot explain the differences in the lattice parameters of the homoepitaxial metal-organic vapor phase epitaxy (MOVPE) layer and HVPE bulk GaN since both have a free-electron concentration below 10^{17} cm^{-3}. The differences of 0.0009 and 0.002 Å between the *a* and *c* lattice parameters of HP GaN and the homoepitaxial MOVPE GaN layer, respectively, are well explained by the deformation potential and size effects related to the high O concentration in the HP GaN.[4,6] Note that the homoepitaxial layer is strained when it is pseudomorphically grown on the HP GaN.[4] It is plausible to estimate the strain-free lattice parameters of GaN assuming a certain relaxation for the homoepitaxial MOVPE layer. However, the previously estimated relaxed lattice parameters[4,6] (also shown in Fig. 2) suffer from the uncertainties in the elastic constants and differ between each other depending on the assumption made. In addition, different defect microstructures apart from the dislocations may also contribute to the observed differences.

Further, the relative change between the lattice parameters of the HVPE bulk and the high- (low-) conductivity HP GaN samples is −0.008% (−0.05%) for the *a* and 0.02% (−0.01%) for the *c* lattice parameter. This finding indicates an anisotropic nature of the involved effect(s) on the lattice parameters and suggests that complex or extended defects might be responsible. Despite the superior crystal and optical quality of the HVPE-GaN material, the dislocation density is still at least two orders of magnitude higher compared to the HP GaN. In principle, interaction of point defects with dislocations may give rise to complex/anisotropic effect on the material lattice parameters. The lattice parameters of the HVPE bulk GaN may also be affected by the presence of so-called intrinsic (*growth*) strain due to the epitaxial nature of the growth.[16] A small tensile stress of 0.1–0.3 GPa, attributed to grain coalescence, has been measured at the growth temperature for MOVPE GaN films on sapphire.[17] However, the presence of such a tensile intrinsic strain in the HVPE material may contribute but cannot explain alone the observed differences in the lattice parameters since it should lead to a contraction of the *c* lattice parameter because of the biaxial nature of the strain. On the other hand, the HVPE and HP GaN bulk material may have different elastic properties stemming from different defect structures and growth peculiarities. Consequently, this may lead to different paths of the thermal strain relaxation in the two types of bulk GaN material during the cooling down from the growth to room temperature, possibly accounting for the observed difference in the lattice parameters.

In summary, we have precisely determined the lattice parameters of low-defect density, undoped HVPE bulk GaN material to be $c=5.18523$ Å and $a=3.18926$ Å. These values were shown to be representative for state-of-the-art bulk material fabricated by HVPE. A comparison between HVPE bulk GaN with HP bulk GaN and MOVPE homoepitaxial GaN shows substantial differences in the lattice parameters of these materials. The size and deformation potential effects due to common impurities and dopants are excluded as a possible origin of the observed difference, and it is suggested that a difference of the elastic properties or effect of complex or extended defects may be the reason. Further experimental and theoretical investigations are needed to unveil the origin of the observed difference in the lattice parameters. It is important to note that the concept of universal strain-free lattice parameters is still not applicable to state-of-the-art bulk GaN and caution should be taken when calibrating fundamental material parameters with strain.

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