Effects of Miscut of Prestructured Sapphire Substrates and MOVPE Growth Conditions on $(11\bar{2}2)$ Oriented GaN

Marian Caliebe

In this work [1], the influence of sapphire mis-orientation on the quality of coalesced $(11\bar{2}2)$ *GaN layers grown on r-plane prestructured sapphire substrates (r-PSS) is investigated. It was found that the angle of the GaN* $(11\bar{2}2)$ *plane towards the surface plane of the sapphire wafer can be adjusted by the mis-orientation of the substrate. Furthermore, we discovered that the c-direction of GaN is tilted by more than* $1°$ *towards the c-direction of the sapphire wafer. Moreover, the influence of the MOVPE growth temperature, V/III ratio and reactor pressure on the coalesced layer has been studied. While a high temperature and small V/III ratio are beneficial, the reactor pressure did not show any significant impact on the crystal quality and surface roughness.*

1. Introduction

While highly efficient blue and red light-emitting diodes (LEDs) are commercially available, yet, there is a lack of efficient LEDs emitting green and yellow light. In literature, this problem is called the "green gap". One possible reason, blamed for this behavior, is the quantum-confined Stark effect. High internal piezo-electric fields separate electrons and holes in the InGaN quantum wells and thus decrease the recombination probability considerably [2–6].

Our approach to reduce the internal field is the use of semipolar $(11\bar{2}2)$ oriented GaN substrates. While there is the possibility to grow $(11\bar{2}2)$ GaN on m-plane sapphire [7], the achievable material quality is poor [8]. Another option is slices, cut from bulk, produced by Hydride Vapor Phase Epitaxy (HVPE). While homoepitaxy permits best results, these substrates are limited in size and are highly expensive [9–11].

Here, the following approach is used: Trenches with a c-plane-like side facet are etched in r-plane sapphire substrates. To prevent growth of a-plane GaN on the $(10\bar{1}2)_{Al_2O_3}$ facet, a SiO_2 layer is deposited by Plasma-Enhanced Chemical Vapor Deposition (PECVD). By Metalorganic Vapor Phase Epitaxy (MOVPE), GaN grows on the c-plane-like facets of the trenches predominantly in c-direction. After a while the individual GaN stripes coalesce to a closed layer. Due to growth in the well established c-direction, a high material quality can be achieved. Also, this method can be easily scaled up, allowing growth on low-priced, large substrates exceeding 100 mm in diameter. It was first demonstrated by Okada et al. [12]. Excellent $(11\bar{2}2)$ GaN layers have also been grown by de Mierry et al. [8] and Leung et al. [13] following this approach.

Typically, such semipolar samples have a fairly large RMS roughness of approximately 50 nm on an area of $50 \times 50\,\mu m^2$. This study was motivated to improve the surface quality. However, by the two attempts described here, we mainly gained other insights. First, the influence of mis-orientation of sapphire wafers has been studied systematically. Then, we searched for proper growth conditions for the GaN layer after coalescence by varying the temperature, V/III ratio and pressure. The impact of the growth temperature and V/III ratio before coalescence has already been studied by Kurisu et al. [14]. However, the focus of their study was to find the optimum growth conditions on a sapphire wafer without any SiO_2 mask and not optimizing the surface quality. By investigating the influence of the growth parameters after coalescence, we want to find optimum conditions for $(11\bar{2}2)$ oriented GaN in particular.

2. Experimental

2.1 Template preparation

All GaN layers are grown on r-plane sapphire substrates (r-PSS). which have been prestructured as described by S. Schwaiger *et al.* [15]. At first, a 200 nm thick SiO_2 mask layer is deposited by PECVD on the bare r-plane sapphire wafer. By conventional photolithography, resist stripes with a period of 6 µm and a width of 3 µm are manufactured and a Ni etch mask is deposited. After lift-off, the trenches are etched by Reactive-Ion Etching (RIE). The remains of the metal mask are removed wet chemically. The average resulting sidewall angle of the c-plane like facet is 75°.

2.2 MOVPE growth

GaN growth by MOVPE is carried out in a commercial Aixtron-200/4 RF-S HT reactor with the precursors TMGa, NH_3 and TMAl. Following our experience on c-plane GaN growth [16], first an AlN:O nucleation layer with an oxygen content of approximately 10% [17] is deposited at 990°C. A GaN buffer layer follows at 1105°C, a V/III ratio of 870 and a reactor pressure of 150 hPa. After 3.5 min, the reactor temperature is decreased to 1025 °C. After growth of approximately 0.5 µm in c-direction on the sidewalls, GaN growth is paused for the *in-situ* deposition of a SiN_x interlayer that is formed with the precursor SiH_4 [18]. Then, GaN growth continues for 105 min at 1025 °C and a V/III ratio of 870 resulting in a total layer thickness of 5.7 µm.

3. Mis-Orientation of the Sapphire Substrate

As calculated in [15], the theoretical angle between the $(11\bar{2}2)_{GaN}$ and $(0001)_{GaN}$ plane is 58.41°, while the angle between the r- and c-plane of the sapphire substrate is only 57.61°. Thus, if we assume that the c-planes of GaN and sapphire are parallel, the theoretical angle of the $(11\bar{2}2)_{GaN}$ plane towards the $(0001)_{GaN}$ plane differs from the angle of the $(10\bar{1}2)_{Al_2O_3}$ plane towards the $(0001)_{Al_2O_3}$ plane by 0.8°. Hence, the $(11\bar{2}2)_{GaN}$ plane is expected to be tilted with respect to the surface (for exactly oriented r-plane sapphire wafers), which might lead to a saw-tooth like coalesced layer and a rough surface (Fig. 1). Using mis-oriented sapphire substrates could compensate this tilt so that the individual GaN stripes can coalesce without height difference. This motivated some other groups to use sapphire wafers with a miscut of 0.5° [12, 14, 19]. Kurisu et al. measured an angle of 0.29° of a macrostep on the surface by Atomic Force Microscopy (AFM), which supports this expectation [14]. However, systematic studies about the influence of various miscut angles on the properties of the final semipolar GaN layer have not yet been reported.

Therefore, we have investigated the influence of the mis-orientation in more detail: For this experiment, we have taken sapphire wafers with a mis-orientation of 0.0°, 0.5°, 1.0° and 1.5° around the a-axis towards the c-direction (Fig. 1). The wafers are patterned and growth is carried out as described above.

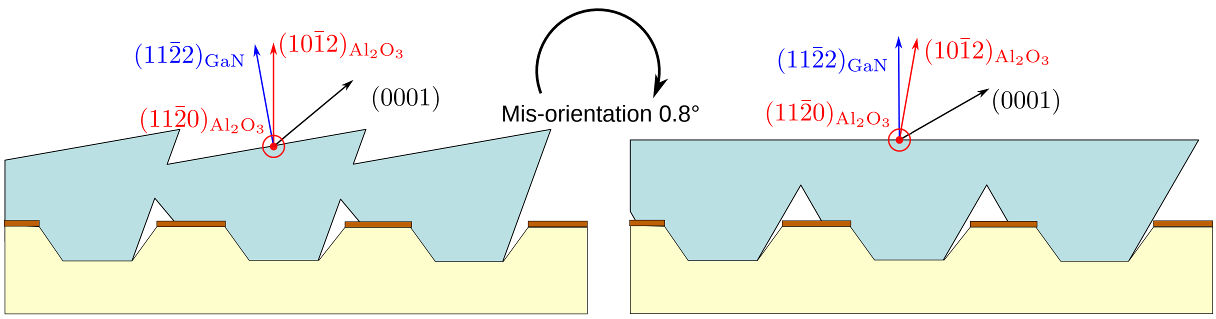

Fig. 1: Hypothesis: By using mis-oriented sapphire wafers the GaN $(11\bar{2}2)$ plane might be aligned parallel to the surface (angles exaggerated).

The crystallographic orientations of the $(11\bar{2}2)_{GaN}$, $(0006)_{GaN}$, $(10\bar{1}2)_{Al_2O_3}$ and $(00012)_{Al_2O_3}$ with respect to each other have been measured by High Resolution X-ray Diffraction (HRXRD) in a Bragg-Brentano configuration. For highest accuracy, ω and 2θ of the planes $(11\bar{2}2)_{GaN}$, $(0006)_{GaN}$ and $(10\bar{1}2)_{Al_2O_3}$ have been determined in an asymmetric scan. Then, the reciprocal space coordinates s_x and s_z of these reflexes have been calculated as described in [20]. From the position in reciprocal space, the angular difference follows directly. However, due to geometric limitations, it is not possible to measure the $(00012)_{Al_2O_3}$ reflex in this way. Therefore, the inclination of the c-planes has been determined by using additional symmetric χ-scans.

As can be seen in Fig. 2 (a), the c-planes of GaN and sapphire are tilted by more than 1° towards each other and are not in parallel as previously assumed. Thus, the $(11\bar{2}2)_{GaN}$ and $(10\bar{1}2)_{Al_2O_3}$ planes are more parallel than the theoretical tilt of 0.8° (Fig. 2 (b)). This results in an offset of the orientation of the $(11\bar{2}2)_{GaN}$ plane towards the wafer surface (Fig. 2 (c)). From this series, the sample without miscut is the one with the most parallel $(11\bar{2}2)_{GaN}$ plane with respect to the wafer surface.

However, the influence of the mis-orientation on the full width at half maximum (FWHM) of the HRXRD rocking curves and surface roughness is almost negligible (Fig. 3). From statistics of several wafers, grown under exactly the same conditions, the error-bar of the HRXRD and AFM measurements has been determined to 10% and 15%, respectively.

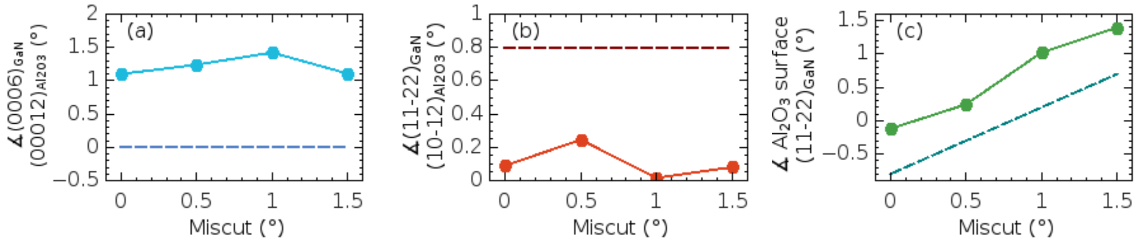

Fig. 2: Measured data and expected angles (dashed line) of tilt between different lattice planes and wafer surface, respectively. (a) Angle between the c-planes of GaN and Al_2O_3. (b) Angle between the $(11\bar{2}2)_{GaN}$ and $(10\bar{1}2)_{Al_2O_3}$ plane. (c) Orientation of the $(11\bar{2}2)_{GaN}$ plane towards the wafer surface plane.

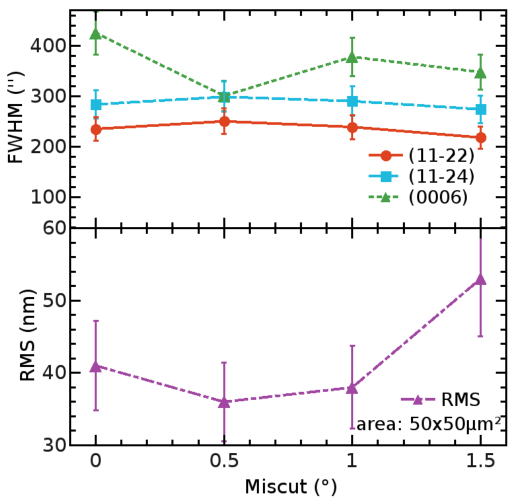

Fig. 3: FWHM of HRXRD rocking curves (top) and surface roughness (bottom) measured by atomic force microscopy (AFM).

Regarding the low-temperature ($T = 13\,\mathrm{K}$) photoluminescence (PL) spectra (Fig. 4), the miscut decreases the intensity of the peak related to the density of basal plane stacking faults (BSF) with respect to the band of the donor bound exciton D^0X, whose FWHM is slightly decreasing as well. From cathodoluminescence measurements (CL) and transmission electron microscopy (TEM) [15, 21], we know that the BSFs are mainly present in the -c-wing and are overgrown by the +c-wing (see also [22, 23]). With an estimated absorption coefficient of $\alpha = 1 \cdot 10^5\mathrm{cm}^{-1}$ [24,25], we obtain a penetration depth of 100 nm only, for our exciting laser beam ($\lambda = 325\,\mathrm{nm}$). Thus, by PL, we only see the BSFs penetrating to the surface.

4. Variation of Growth Parameters of GaN Top Layer

In a next step, we investigated the influence of various growth parameters of the GaN layer after coalescence in order to minimize the surface roughness and improve its crystalline

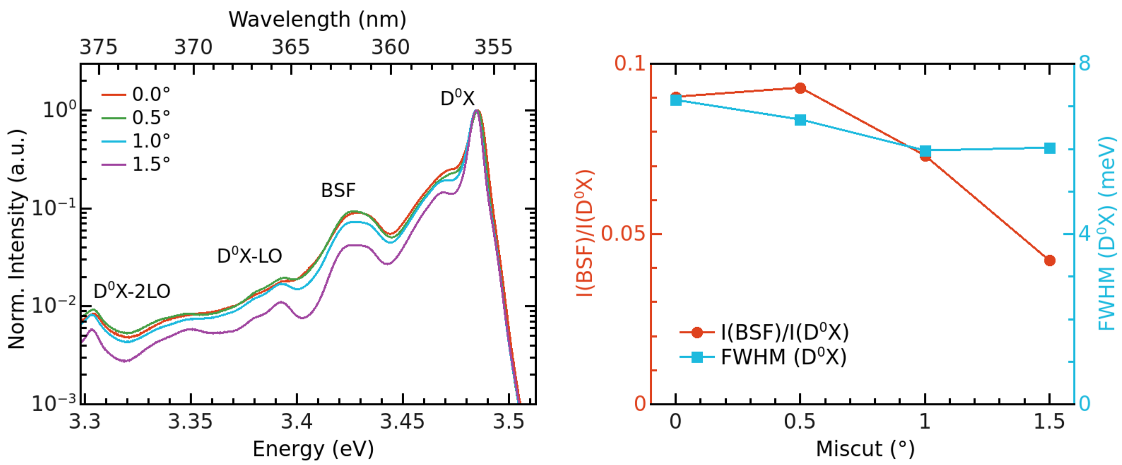

Fig. 4: Left: PL spectra, normalized to the donor-bound excitonic transition D^0X. Right: Ratio of BSF peak and D^0X peak intensities and FWHM of D^0X. The basal plane stacking fault luminescence (BSF) is decreasing with higher miscut.

quality. The samples investigated here are grown on sapphire wafers without miscut and are produced as described in Sect. 2. Here, after the deposition of the SiN_x interlayer, GaN growth continues for only 60 min under the conditions described above. Then, the TMGa flux is increased from 26 sccm to 40 sccm (growth rate increases from 2.9 µm/h to 4.4 µm/h) and growth is continued for another 60 min with several top layer variations. The resulting total layer thickness (measured from the sapphire surface) is approximately 7.9 µm.

Beside the growth temperature and V/III ratio studies that are discussed below, the reactor pressure has been decreased from 150 hPa to 75 hPa in a further experiment. However, there was no observable difference in the crystal quality or surface roughness.

4.1 Temperature variation

When increasing the growth temperature, at a V/III ratio of 565, the BSF luminescence is decreasing, pointing to a reduction of the BSF density (Fig. 5). Moreover, the FWHM of the donor bound exciton signal D^0X becomes narrower and the free exciton band (FE) appears.

While there seems to be a minimum for the surface roughness at 1066 °C (Fig. 6 (bottom)), the FWHM of the HRXRD rocking curves is hardly influenced (Fig. 6 (top)) by the growth temperature. Fig. 7 shows an AFM micrograph of the sample grown at $T = 1066$°C at a V/III ratio of 565. Typical for those samples are the flaky appearance and "arrow-head" shaped elevations.

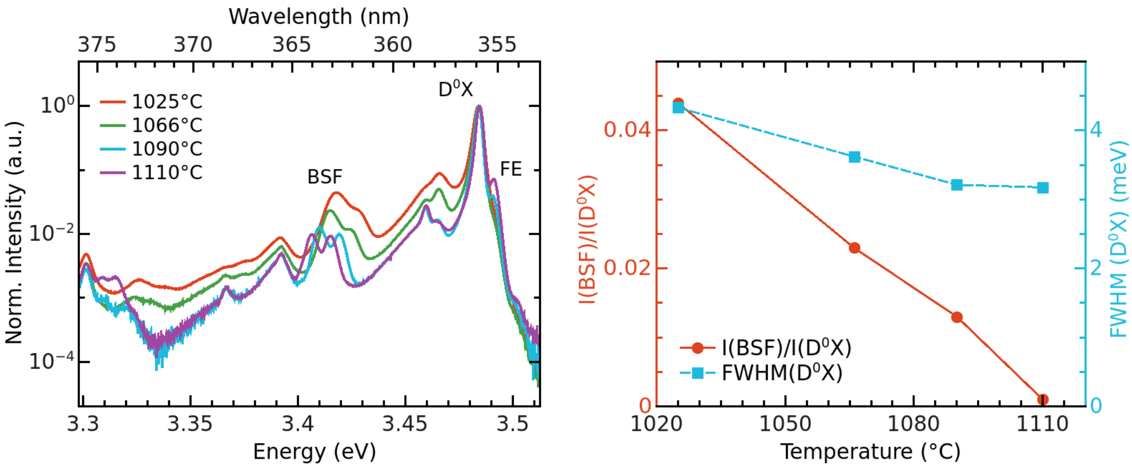

Fig. 5: Normalized PL spectra. The intensity of the basal plane stacking fault related peak (BSF) is decreasing with higher temperature and the FWHM of the D^0X becomes narrower while the band of free excitons (FE) appears.

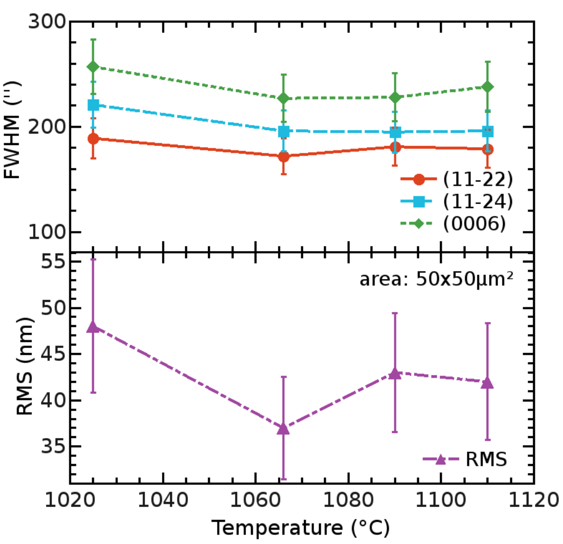

Fig. 6: The growth temperature shows almost no influence on the FWHM of HRXRD rocking curves (top). However, there seems to be a minimum of the surface roughness at 1066 °C (bottom).

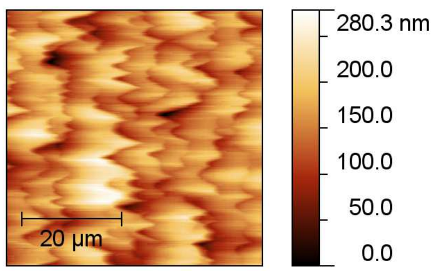

Fig. 7: AFM micrograph of the sample grown at $T = 1066°C$ at a V/III ratio of 565.

4.2 V/III ratio variation

The conditions from the temperature series that led to the smallest surface roughness (f(TMGa) = 40 sccm, T = 1066 °C) were chosen for a subsequent V/III ratio variation, by varying the NH_3 flux. The total gas flux in the reactor has been kept constant by compensating with H_2.

With decreasing V/III ratio, the intensity of the BSF related peak and the FWHM of the D^0X become smaller and the free exciton band (FE) emerges (Fig. 8). Also, both the FWHM of HRXRD rocking curves and the surface roughness improve for V/III ratios around 150 (Fig. 9).

The slightly larger RMS values of this series (Fig. 9), as compared to the temperature series (Fig. 6), are probably caused by small process fluctuations in sapphire structuring and MOVPE growth in not subsequently manufactured samples.

5. Summary

These studies show that the orientation of the $(11\bar{2}2)_{\mathrm{GaN}}$ plane towards the wafer surface can be adjusted by using sapphire wafers with miscut. However, we observed that the c-plane of GaN is tilted by more than 1° towards the c-plane of the sapphire template on all wafers. Thus, for sapphire wafers without mis-orientation, the $(11\bar{2}2)_{\mathrm{GaN}}$ plane is already parallel to the surface. While the PL spectra can be interpreted as slight improvements of the crystal quality with increasing wafer miscut, there is hardly any change visible in HRXRD and AFM.

In experiments with various top layer growth conditions, we found that a high growth temperature above 1066 °C and moderate V/III ratio of 150 seems to be beneficial for

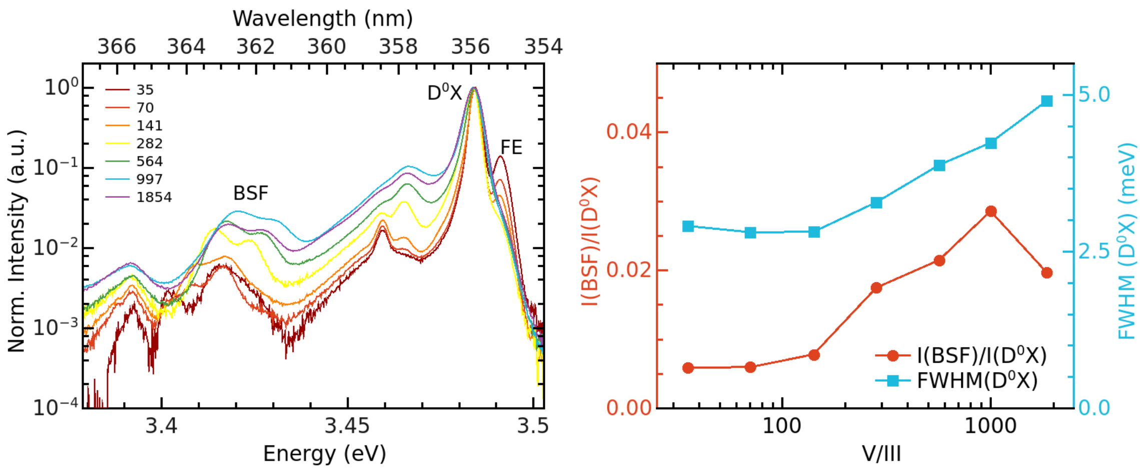

Fig. 8: Left: Normalized PL spectra. The band of free excitons (FE) appears at a small V/III ratio. Right: The basal plane stacking fault luminescence (BSF) and the FWHM of the D^0X are decreasing with smaller V/III ratio.

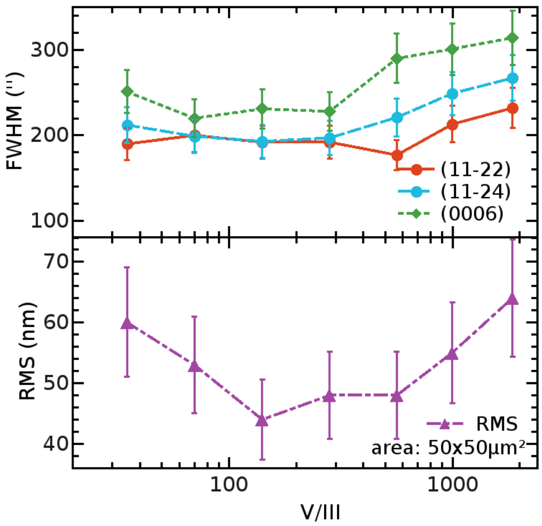

Fig. 9: Top: FWHM of HRXRD rocking curves. Bottom: Surface roughness measured by AFM.

crystal quality and surface roughness. However, the surface roughness can not be improved considerably by varying the growth parameters of the coalesced layers only.

Acknowledgment

I thank the coauthors of this article [1] T. Meisch and F. Scholz of the Institute of Optoelectronics at Ulm University and M. Madel of the Institute of Quantum Matter, Semiconductor Physics Group at Ulm University for their scientific support. We gratefully acknowledge the support of K. Thonke of the Institute of Quantum Matter, Semiconductor Physics Group, in interpreting the PL spectra. For their technical contribution, we thank R. Rösch, C. Steinmann and Z. Cheng of the Institute of Optoelectronics. This work was financially supported by the European Commission (FP7) within the framework of the project "AlGaInN materials on semi-polar templates for yellow emission in solid state lighting applications" (ALIGHT).

References

[1] M. Caliebe, T. Meisch, M. Madel, and F. Scholz, "Effects of miscut of prestructured sapphire substrates and MOVPE growth conditions on (11$\bar{2}$2) oriented GaN", *J. Cryst. Growth*, vol. 414, pp. 100–104, 2015.

[2] F. Scholz, T. Wunderer, B. Neubert, F. Feneberg, and K. Thonke, "GaN-based light-emitting diodes on selectively grown semipolar crystal facets", *MRS Bulletin*, vol. 34, pp. 328–333, 2009.

[3] T. Takeuchi, H. Amano, and I. Akasaki, "Theoretical study of orientation dependence of piezoelectric effects in wurtzite strained GaInN/GaN heterostructures and quantum wells", *Jpn. J. Appl. Phys.*, vol. 39, pp. 413–416, 2000.

[4] F. Bernardini, V. Fiorentini, and D. Vanderbilt, "Spontaneous polarization and piezoelectric constants of III-V nitrides", *Phys. Rev. B*, vol. 56, pp. R10024–R10027, 1997.

[5] O. Ambacher, "Growth and applications of group III-nitrides", *J. Phys. D: Appl. Phys.*, vol. 31, pp. 2653–2710, 1998.

[6] A.E. Romanov, T.J. Baker, S. Nakamura, and J.S. Speck, "Strain-induced polarization in wurtzite III-nitride semipolar layers", *J. Appl. Phys.*, vol. 100, pp. 023522-1–10, 2006.

[7] T.J. Baker, B.A. Haskell, F. Wu, J.S. Speck, and S. Nakamura, "Characterization of planar semipolar gallium nitride films on sapphire substrates", *Jpn. J. Appl. Phys.*, vol. 45, pp. L154–L157, 2006.

[8] P. de Mierry, N. Kriouche, M. Nemoz, S. Chenot, and G. Nataf, "Semipolar GaN films on patterned r -plane sapphire obtained by wet chemical etching", *Appl. Phys. Lett.*, vol. 96, pp. 231918-1–3, 2010.

[9] M. Ueda, K. Kojima, M. Funato, Y. Kawakami, Y. Narukawa, and T. Mukai, "Epitaxial growth and optical properties of semipolar (11-22) GaN and InGaNâGaN quantum wells on GaN bulk substrates", *Appl. Phys. Lett.*, vol. 89, pp. 211907-1–3, 2006.

[10] K. Fujito, S. Kubo, and I. Fujimura, "Development of bulk GaN crystals and nonpolar/semipolar substrates by HVPE", *MRS Bull.*, vol. 34, pp. 313–317, 2009.

[11] F. Scholz, "Semipolar GaN grown on foreign substrates: a review", *Semicond. Sci. Technol.*, vol. 27, pp. 024002-1–15, 2012.

[12] N. Okada, A. Kurisu, K. Murakami, and K. Tadatomo, "Growth of semipolar (11-22) GaN layer by controlling anisotropic growth rates in r -plane patterned sapphire substrate", *Appl. Phys. Express*, vol. 2, pp. 091001-1–3, 2009.

[13] B. Leung, Q. Sun, C. Yerino, Y. Zhang, J. Han, B.H. Kong, H.K. Cho, K.Y. Liao, and Y.L. Li, "Growth evolution and microstructural characterization of semipolar $(11\bar{2}2)$ GaN selectively grown on etched r-plane sapphire", *J. Cryst. Growth*, vol. 341, pp. 27–33, 2012.

[14] A. Kurisu, K. Murakami, Y. Abe, N. Okada, and K. Tadatomo, "Characterization of semipolar $(11\bar{2}2)$ GaN on c-plane sapphire sidewall of patterned r-plane sapphire substrate without SiO_2 mask", *Phys. Status Solidi C*, vol. 7, pp. 2059–2062, 2010.

[15] S. Schwaiger, S. Metzner, T. Wunderer, I. Argut, J. Thalmair, F. Lipski, M. Wieneke, J. Bläsing, F. Bertram, J. Zweck, A. Krost, J. Christen, and F. Scholz, "Growth and coalescence behavior of semipolar $(11\bar{2}2)$ GaN on pre-structured r-plane sapphire substrates", *Phys. Status Solidi B*, vol. 248, pp. 588–593, 2011.

[16] J. Hertkorn, P. Brückner, S.B. Thapa, T. Wunderer, F. Scholz, M. Feneberg, K. Thonke, R. Sauer, M. Beer, and J. Zweck, "Optimization of nucleation and buffer layer growth for improved GaN quality", *J. Cryst. Growth*, vol. 308, pp. 30–36, 2007.

[17] J. Bläsing, A. Krost, J. Hertkorn, F. Scholz, L. Kirste, A. Chuvilin, and U. Kaiser, "Oxygen induced strain field homogenization in AlN nucleation layers and its impact on GaN grown by metal organic vapor phase epitaxy on sapphire: An x-ray diffraction study", *J. Appl. Phys.*, vol. 105, pp. 033504-1–9, 2009.

[18] M. Caliebe, T. Meisch, B. Neuschl, S. Bauer, J. Helbing, D. Beck, K. Thonke, M. Klein, D. Heinz, and F. Scholz, "Improvements of MOVPE grown $(11\bar{2}2)$ oriented GaN on pre-structured sapphire substrates using a SiN_x interlayer and HVPE overgrowth", *Phys. Status Solidi C*, vol. 11, pp. 525–529, 2014.

[19] H. Furuya, Y. Hashimoto, K. Yamane, N. Okada, and K. Tadatomo, "Characterization of {11-22} GaN grown using two-step growth technique on shallowly etched r-plane patterned sapphire substrates", *J. Cryst. Growth*, vol. 391, pp. 41–45, 2014.

[20] M.A. Moram and M.E. Vickers, "X-ray diffraction of III-nitrides", *Rep. Prog. Phys.*, vol. 72, pp. 036502-1–40, 2009.

[21] Y. Han, M. Caliebe, T. Meisch, M. Pristovsek, M. Kappers, F. Scholz, and C. Humphreys, "Structural characterisation of semi-polar GaN templates grown on pre-structured r-plane sapphire substrates", in *15th European Workshop on Metalorganic Vapour Phase Epitaxy (EWMOVPE XV), June 2-5, 2013, Aachen, Germany, Extended Abstracts*, pp. 55–58, Forschungszentrum Jülich GmbH, 2013.

[22] N. Kriouche, M. Leroux, P. Vennéguès, M. Nemoz, G. Nataf, and P. de Mierry, "Filtering of defects in semipolar (11-22) GaN using 2-steps lateral epitaxial overgrowth", *Nanoscale Res. Lett.*, vol. 5, pp. 1878–1881, 2010.

[23] B. Lacroix, M.P. Chauvat, P. Ruterana, G. Nataf, and P. de Mierry, "Efficient blocking of planar defects by prismatic stacking faults in semipolar (11-22)-GaN layers on m-sapphire by epitaxial lateral overgrowth", *Appl. Phys. Lett.*, vol. 98, pp. 121916-1–3, 2011.

[24] J.F. Muth, J.H. Lee, I.K. Shmagin, R.M. Kolbas, H.C. Casey Jr., B.P. Keller, U.K. Mishra, and S.P. DenBaars, "Absorption coefficient, energy gap, exciton binding energy, and recombination lifetime of GaN obtained from transmission measurements", *Appl. Phys. Lett.*, vol. 71, pp. 2572–2574, 1997.

[25] R. Dingle, D.D. Sell, S.E. Stokowski, P.J. Dean, and R.B. Zetterstrom, "Absorption, reflectance, and luminescence of GaN single crystals", *Phys. Rev. B*, vol. 3, pp. 497–500, 1971.