Parasitic Background Doping in Semipolar GaN

Marian Caliebe and Ferdinand Scholz

Semipolar GaN layers grown by metalorganic vapor phase epitaxy typically show quite strong n-type background doping, mainly caused by parasitic oxygen incorporation. In the studies reported here, we have investigated how to influence this parasitic doping by varying the growth temperature and the V-III ratio. Moreover, direct correlation with other sample properties, particularly the surface roughness, has been observed. Surprisingly, thick semipolar GaN layers grown by hydride vapor phase epitaxy exhibit very high background doping at the interface to the template and at the surface, whereas the carrier concentration seems to be significantly lower in the main part of the bulk layer.

1. Introduction

Semipolar GaN layers and respective heterostructures have attracted strong interest over the recent years (see, e.g., [1, 2] and references therein) as possible solutions to the so-called 'green-gap problem', i.e., the decrease of the LED efficiency when the color of the emitted light is shifted from blue to green. A major part of this problem is considered to be caused by the internal piezoelectric field in the active GaInN quantum wells of conventional structures grown in the polar *c*-direction, being larger for higher In content as needed for longer wavelength emission. In contrast, semipolar layers are grown in other, less polar directions leading to strongly reduced piezoelectric fields. However, in spite of these research activities, semipolar LEDs could not yet outperform their polar counterparts (see, e.g., results obtained in our recent research group PolarCoN [3] and in our EC project ALIGHT [4]). Typically, the lower quality of semipolar structures is blamed for this deficiency. In particular, a high basal plane stacking fault (BSF) density is to emphasize as the main difference to conventional *c*-plane structures. Moreover, a significantly higher background carrier concentration above $10^{18}\,\mathrm{cm}^{-3}$ is observed in nominally undoped semipolar GaN layers [5, 6]. In the studies presented here, we have investigated by which growth parameters these concentrations can be influenced and eventually reduced. Besides parameters like temperature or V-III ratio, also the surface roughness of the layers seem to play an important role.

2. Experimental

The semipolar layers investigated here are grown on stripe-patterned sapphire wafers as described previously [7]. In brief, this procedure is described as follows: Few micrometer wide stripe trenches are dry-etched in specifically oriented sapphire wafers having inclined *c*-plane-like side-facets. These side-facets are the nucleation sites for the GaN growth performed in an Aixtron AIX-200/4 RF-S HT low-pressure horizontal metalorganic vapor phase epitaxy (MOVPE) reactor. After having grown out of the trenches — basically growing along the inclined *c*-direction —, the GaN stripes eventually coalesce forming a layer with semipolar surface. For a $(11\bar{2}2)$ surface, sapphire wafers with *r*-plane orientation have been used. We have optimized this process carefully (see, e.g. [8]) achieving dislocation densities below $10^8\,\text{cm}^{-2}$ and BSF densities of $200\,\text{cm}^{-1}$. Here, we focus mainly on the electrical and other properties of the top layer having a typical thickness of 2–3 µm grown on an about 5 µm thick multi-layer buffer structure [7]. Thicker layers up to several 100 µm have been deposited on these templates by hydride vapor phase epitaxy [9].

Carrier concentrations have been determined by C-V measurements. Moreover, the oxygen content was evaluated by secondary ion mass spectrometry (SIMS)[2]. Low-temperature photoluminescence (PL) and scanning electron microscopy based cathodoluminescence (CL)[3] spectra have been analyzed with respect to carrier concentration and defects like stacking faults. The surface roughness was determined by atomic force microscopy (AFM).

3. Results and Discussion

3.1 Variation of growth parameters

In order to find relations between the parasitic background doping and the growth procedure, we have grown several series of samples. As reference, we take conditions which have been optimized for *c*-plane growth and slightly modified in order to get best crystalline quality of semipolar layers [7]. As mentioned above, we found quite high background doping concentrations of about $7 \cdot 10^{17}\,\text{cm}^{-3}$ for these conditions ($T = 1041\,°\text{C}$, V-III $\simeq 560$), whereas comparable *c*-plane layers show concentrations below $1 \cdot 10^{17}\,\text{cm}^{-3}$.

When increasing the growth temperature, we observed a significant decrease of the carrier concentration (Fig. 1). SIMS data of the oxygen concentration in some of these layers show the same trend confirming that indeed oxygen is the main impurity in these layers. This trend is often observed in MOVPE grown layers [10]. However, when decreasing the temperature below 1000 °C, we also observed a decrease of carrier concentration and oxygen content [11]. Obviously, a maximum oxygen uptake happens around 1000 °C.

The NH_3 flow and hence the V-III ratio is another growth parameter expected to significantly influence the background doping. Indeed, we observed a distinct decrease of the carrier concentration with decreasing V-III ratio, again nicely accompanied by a respective decrease of the O concentration as detected by SIMS. These data suggest that NH_3 may be a source of oxygen, although we have used best quality NH_3 with a purity of 6.0.

3.2 Influence of surface roughness on background doping?

Besides the above-mentioned growth parameters, it seems that also the surface roughness of our $(11\bar{2}2)$ layers influences the parasitic incorporation of n-type impurities like oxygen.

[2]SIMS evaluation was performed by RTG Mikroanalyse GmbH, Berlin.
[3]CL measurements have been done by M. Hocker *et al.*, Inst. of Quantum Matter, Ulm University.

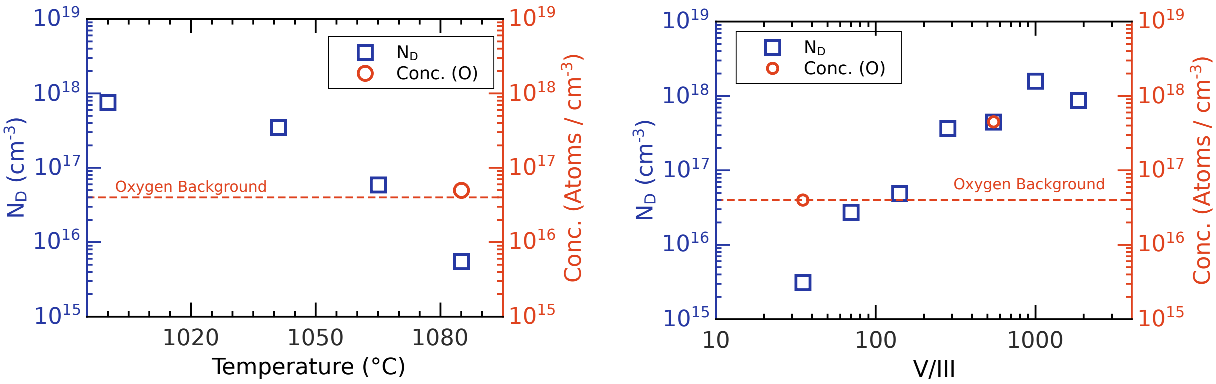

Fig. 1: Carrier concentration in $(11\bar{2}2)$ layers determined by C-V measurements as a function of growth temperature (V-III = 564, left) and V-III ratio ($T = 1041\,°\mathrm{C}$, right).

Layers with different surface roughness have been obtained by varying the sapphire trench period. Such studies have been performed to find the optimum periodicity for our growth procedure [12]. Analyzing low temperature PL spectra of this series, we observed that the intensity ratio between the donor-bound exciton (D^0,X) and the free exciton (X_A) lines correlate perfectly with the absolute intensity of the (D^0,X) line and even with the surface roughness measured by AFM (Fig. 2). This ratio is a qualitative indication of the donor density. Therefore, we also performed C-V measurements on these samples. Indeed, the donor concentration coincides also with the roughness data. This may be explained by the strong oxygen sensitivity of a perfect $(11\bar{2}2)$ plane, whereas other planes (being present in rougher surfaces) incorporate less oxygen.

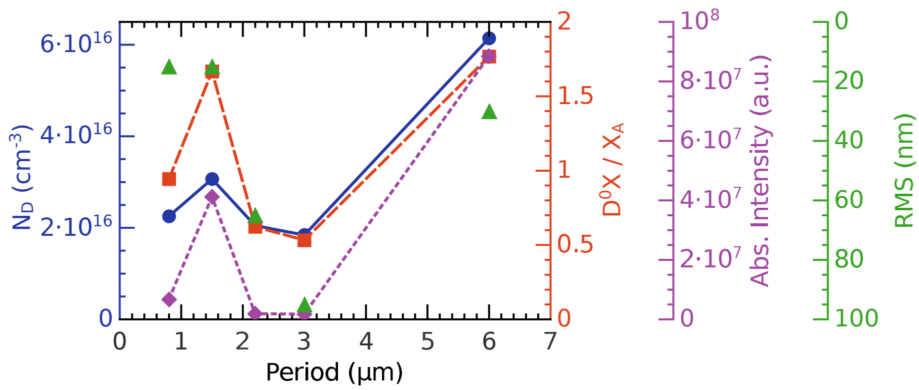

Fig. 2: Donor concentration, intensity ratio of (D^0,X) and (X_A) PL lines, absolute intensity, and surface roughness plotted versus stripe period of our sample series where the latter was varied between 0.8 and 6 µm.

3.3 Background doping in HVPE-grown semipolar layers

Previous low-temperature PL measurements on our HVPE-grown $(11\bar{2}2)$ layers have shown the presence of a so-called "free electron recombination band" (FERB) broadening the typically very sharp (D^0X) peak and extending it particularly to higher energies [13]. This is consistent with very high n-type background doping concentrations in the $10^{19}\,\mathrm{cm}^{-3}$ range for the near-surface volume probed by PL, whereas comparable *c*-plane layers always exhibit carrier concentrations in the mid $10^{16}\,\mathrm{cm}^{-3}$ range [14]. Such high carrier concentrations have also been confirmed by van der Pauw Hall experiments which yield average values for the whole layers.

In order to check details of such parasitic background doping in these layers, we have analyzed the cross-section of a $(11\bar{2}2)$ layer grown by HVPE on top of an MOVPE grown buffer as discussed above up to a total thickness of approximately 300 µm. Details of this growth procedure have been published in [9]. This sample was grown with a growth rate of about 100 µm/h.

Local luminescence spectra have been obtained by SEM-based CL at $T \approx 10\,\mathrm{K}$. Surprisingly, we observed quite sharp peaks over most of the cross-section indicating a lower carrier concentration, while the FERB dominated near the MOVPE-HVPE interface and close to the upper sample surface. By analyzing the shape of these peaks[4], the local carrier concentration can be deduced, as depicted in Fig. 3. These data could be confirmed and further quantified by analyzing the luminescence peak position of the signal of the basal plane stacking fault I_1 which was found to be sensible to the carrier concentration [15]. Indeed, fairly low carrier concentrations around $10^{18}\,\mathrm{cm}^{-3}$ can be deduced from those spectra in the main bulk region between lower interface and upper surface.

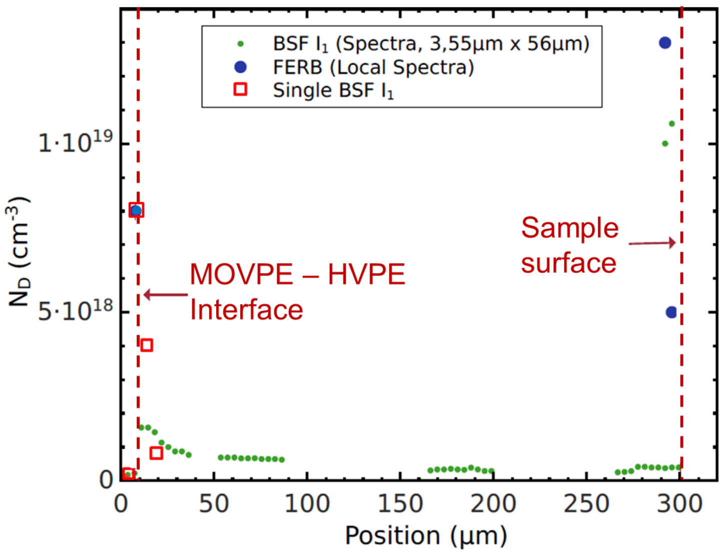

Fig. 3: Donor concentration profile over the cross-section of a semipolar GaN layer with a thickness of about 300 µm, determined by various methods (see text).

4. Conclusion

We have investigated the parasitic background doping in semipolar $(11\bar{2}2)$ GaN layers grown by MOVPE and HVPE. In both cases, we find high background doping, obviously

[4]Performed by M. Hocker and K. Thonke, Inst. of Quantum Matter, Ulm University.

due to parasitic oxygen incorporation. This is assumed to be a consequence of the chemical properties of such surface, being more nitrogen-polar than a conventional GaN layer grown in *c*-direction and hence being Ga-polar. Indeed, nitrogen-polar layers are known to incorporate oxygen much more efficiently than Ga-polar layers [16, 17]. For MOVPE-grown semipolar layers, the background doping can be significantly reduced by varying the growth temperature or decreasing the V-III ratio. In HVPE grown layers, fair carrier concentrations have been found in the bulk region with much higher concentrations incorporated at the beginning and at the end of the growth. At the beginning, this may be due to oxygen or water deposits on the surface of the template when transporting it from the MOVPE machine to the HVPE reactor. However, further studies are required to find good explanations for the very high concentrations at the end of growth.

Acknowledgment

We are grateful to M. Hocker and K. Thonke (Inst. of Quantum Matter, Ulm University) for CL evaluations and to N. Hibst (Inst. of Electronic Devices and Circuits, Ulm University) for his help concerning the C-V measurements. S. Tandukar, Z. Cheng (Inst. of Optoelectronics) and A. Plettl (Inst. of Solid State Physics, Ulm University) assisted to realize the sub-micrometer stripe period structures. Moreover, our thanks go to RTG Mikroanalyse GmbH for SIMS analysis.

References

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

[2] F. Scholz, M. Caliebe, G. Gahramanova, D. Heinz, M. Klein, R.A.R. Leute, T. Meisch, J. Wang, M. Hocker, and K. Thonke, "Semipolar GaN-based heterostructures on foreign substrates", *Phys. Status Solidi B*, vol. 253, pp. 13–22, 2016.

[3] "Polarization field control in nitride light emitters", F. Scholz and U. Schwarz (Eds.), pp. 3–185, *Phys. Status Solidi B*, Jan. 2016.

[4] B. Corbett, Z. Quan, D.V. Dinh, G. Kozlowski, D. O'Mahony, M. Akhter, S. Schulz, P. Parbrook, P. Maaskant, M. Caliebe, M. Hocker, K. Thonke, F. Scholz, M. Pristovsek, Y. Han, C.J. Humphreys, F. Brunner, M. Weyers, T.M. Meyer, and L. Lymperakis, "Development of semipolar (11-22) LEDs on GaN templates", H. Jeon, L.W. Tu, M.R. Krames, and M. Strassburg (Eds.), Proc. SPIE 9768, pp. 97681G-1–9, 2016.

[5] S.C. Cruz, S. Keller, T.E. Mates, U.K. Mishra, and S.P. DenBaars, "Crystallographic orientation dependence of dopant and impurity incorporation in GaN films grown by metalorganic chemical vapor deposition", *J. Cryst. Growth*, vol. 311, pp. 3817–3823, 2009.

[6] T. Zhu, D. Sutherland, T.J. Badcock, R. Hao, M.A. Moram, P. Dawson, M.J. Kappers, and R.A. Oliver, "Defect reduction in semi-polar $(11\bar{2}2)$ gallium nitride grown using epitaxial lateral overgrowth", *Jpn. J. Appl. Phys.*, vol. 52, pp. 08JB01-1–5, 2013.

[7] M. Caliebe, Y. Han, M. Hocker, T. Meisch, C. Humphreys, K. Thonke, and F. Scholz, "Growth and coalescence studies of $(11\bar{2}2)$ oriented GaN on pre-structured sapphire substrates using marker layers", *Phys. Status Solidi B*, vol. 253, pp. 46–53, 2016.

[8] 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.

[9] 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.

[10] B. Chung and M. Gershenzon, "The influence of oxygen on the electrical and optical properties of GaN crystals grown by metalorganic vapor phase epitaxy", *J. Appl. Phys.*, vol. 72, pp. 651–659, 1992.

[11] F. Scholz, T. Meisch, and K. Elkhouly, "Efficiency studies on semipolar GaInN-GaN quantum well structures", *Phys. Status Solidi A*, vol. 213, pp. 3117–3121, 2016.

[12] M. Caliebe, S. Tandukar, Z. Cheng, M. Hocker, Y. Han, T. Meisch, D. Heinz, F. Huber, S. Bauer, A. Plettl, C. Humphreys, K. Thonke, and F. Scholz, "Influence of trench period and depth on MOVPE grown GaN on patterned r-plane sapphire substrates", *J. Cryst. Growth*, vol. 440, pp. 69–75, 2016.

[13] P. Schustek, M. Hocker, M. Klein, U. Simon, F. Scholz, and K. Thonke, "Spectroscopic study of semipolar (11-22)-HVPE GaN exhibiting high oxygen incorporation", *J. Appl. Phys.*, vol. 116, pp. 163515-1–9, 2014.

[14] F. Lipski, T. Wunderer, S. Schwaiger, and F. Scholz, "Fabrication of freestanding 2"-GaN wafers by hydride vapour phase epitaxy and self-separation during cooldown", *Phys. Status Solidi A*, vol. 207, pp. 1287–1291, 2010.

[15] M. Hocker, I. Tischer, B. Neuschl, K. Thonke, M. Caliebe, M. Klein, and F. Scholz, "Stacking fault emission in GaN: influence of n-type doping", *J. Appl. Phys.*, vol. 119, pp. 185703-1–6, 2016.

[16] M. Sumiya, K. Yoshimura, K. Ohtsuka, and S. Fuke, "Dependence of impurity incorporation on the polar direction of GaN film growth", *Appl. Phys. Lett.*, vol. 76, pp. 2098–2100, 2000.

[17] N.A. Fichtenbaum, T.E. Matesa, S. Keller, S.P. DenBaars, and U.K. Mishra, "Impurity incorporation in heteroepitaxial N-face and Ga-face GaN films grown by metalorganic chemical vapor deposition", *J. Cryst. Growth*, vol. 310, pp. 1124–1131, 2008.