Wafer Bow of Freestanding GaN Substrates Grown by Hydride Vapor Phase Epitaxy

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Free-standing GaN wafers grown by hydride vapor phase epitaxy are typically concavely bowed. In situ *and* ex situ *curvature measurements indicate that some strain developing at the very beginning of the epitaxial process or even in the template grown by metalorganic vapor phase epitaxy may be the origin of this bow. It can be only partly released by etching the defective back-side of the samples indicating that the strong dislocation density gradient is not the only reason for strain in free-standing GaN.*

1. Introduction

GaN-based light emitting diodes are flooding the consumer market as they recently have reached excellent efficiencies [1]. For such LEDs, still foreign substrates like sapphire are the substrate of choice owing to their cheap price and their excellent availability in large amounts and best quality, although high threading dislocation densities in the range of at least $10^8\,\mathrm{cm}^{-2}$ must be accepted as a consequence of the substantial lattice mismatch between GaN layer and substrate. However, such huge defect densities are not acceptable for GaN based laser diodes, causing short lifetimes of these devices driven at comparably large current densities. For lower defect densities, GaN substrates are required which enable a homo-epitaxial solution. Due to the high melting point and huge equilibrium vapor pressure of GaN, it cannot be grown easily as a bulk substrate.

Therefore, different approaches have been developed over the recent years to realize low-defect-density GaN wafers. The simplest and most successful approach makes use of hydride vapor phase epitaxy (HVPE), where growth rates of several $100\,\mu\mathrm{m/h}$ and hence layers of several mm thickness can be obtained. This process also starts on foreign substrates causing several problems which are not yet solved completely. Fortunately, the above mentioned high dislocation density incorporated into these wafers at the beginning of growth is reduced to values below $10^6\,\mathrm{cm}^{-2}$ at the final surface due to dislocation annihilation processes [2], which is well acceptable for laser diodes. However, the large difference of the thermal expansion coefficients leads to a huge strain during cool-down of the wafer after epitaxy, which for several hundred micrometer thick layers cannot be accommodated elastically and typically causes cracking of the GaN layer into many small pieces. By a careful process optimization, the strain can be used to trigger a self-separation process resulting in free-standing GaN wafers (see, e.g. [3]).

After the substrate removal, the thick GaN wafers are expected to be stress-free. However, surprisingly such free-standing wafers typically are significantly bowed (c.f. [4]) making

further device epitaxy and processing difficult. Although commercially available wafers are typically polished to provide a flat surface, the bowing is still visible by a radially varying inclination of the lattice planes with respect to the flat surface. This will mask procedures where a slight mis-orientation of the wafer leads to optimized epitaxial results.

In order to understand this bow and eventually get inherently flat free-standing GaN layers with unbowed crystal planes, we have investigated the curvature and strain of HVPE grown GaN layers in a wide thickness range, its development during the epitaxial process and possible methods which might influence the wafer bow afterwards.

2. Experimental

The HVPE-growth was performed on templates grown in an Aixtron 200/4 RF-S metal organic vapor phase epitaxy (MOVPE) system on (0001) sapphire with a miscut of 0.3 ° towards the a-plane, a thickness of 430 µm and a diameter of 2". For defect-reduction an *in situ* SiN_x-layer was deposited during the growth of the GaN-buffer [5]. On these templates, a SiN_x layer was deposited *ex situ* by plasma-enhanced chemical vapor deposition (PE-CVD) and processed into a honeycomb-like mask structure by conventional lithography and dry etching in order to facilitate self-separation of the thick GaN layers grown later on these structures by HVPE [3]. Then, the samples were put back into the MOVPE system to initiate lateral growth starting from the open trenches in the mask partly covering the masked area. Although this step could also be done in the later HVPE growth, we preferred to include this extra MOVPE growth which provided a more reliable high quality overgrowth of the masked samples. Then, the samples were loaded into our HVPE reactor, a commercial Aixtron single-wafer HVPE system with a horizontal quartz reactor heated by a five zones furnace. Here, we applied our standard growth conditions as described earlier [3, 6] using ammonia and GaCl, formed *in situ* by streaming HCl gas over a liquid elemental Ga source, as N and Ga precursors, respectively. We adjusted the growth rates to be about 100 µm/h at 1050 °C. Thin layers remained connected to the sapphire wafer, whereas GaN layers with thicknesses above about 500 µm cracked off the substrate along the structured SiN_x mask layer resulting in free-standing GaN samples. The resulting GaN layers showed excellent properties with very sharp spectral lines in high resolution x-ray diffraction, low temperature photoluminescence (donor-bound excitonic line below 500 µeV) and low dislocation densities (below $10^6\,cm^{-2}$ for the mm-thick layers) [3].

For *in situ* measurements of the curvature, a LayTec EpiCurve sensor was adapted to our HVPE system where much higher bowing of the wafers is expected as compared to MOVPE reactors. Unfortunately, such *in situ* measurements could only be performed up to GaN thicknesses of 50–80 µm, because the surface of HVPE layers typically get increasingly bumpy degrading the quality of the reflected laser beams of the curvature sensor and eventually preventing the determination of their distance. The curvature of the layers was also measured *ex situ* after growth by comparing the x-ray diffraction peak angles of several slightly different positions on the samples. Hence the bowing of the crystal planes could be directly determined irrespective of any thickness variations which might disturb optical curvature measurements. The strain in the samples at the final

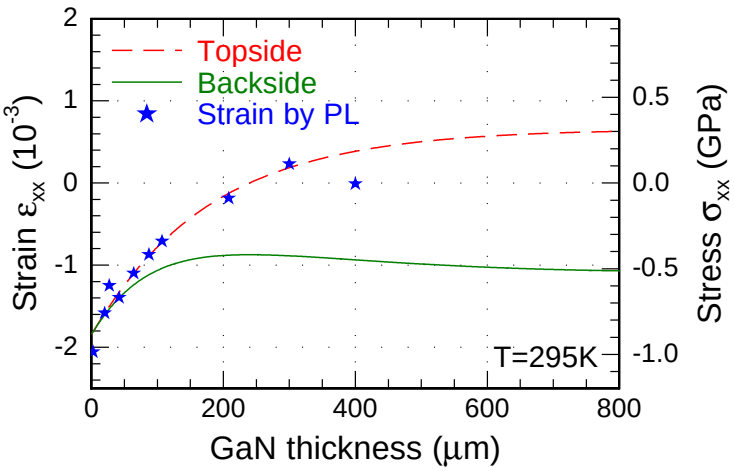

Fig. 1: Room temperature calculated in-plane strain (left axis) and stress (right axis) of GaN layers of various thicknesses grown on a 430 µm thick sapphire wafer at the GaN surface (broken red line) and at the layer-substrate interface (full green line) as compared to data measured by low temperature PL (blue stars).

surface could additionally be determined from the position of the donor-bound excitonic line measured by low-temperature photoluminescence (PL; $T \approx 15$ K) following the data published by Fu et al. [7]. The *ex situ* measurements have been typically performed on small pieces of the 2" wafers comparable in size and shape which we assumed to be spherically bowed, whereas the curvature of strongly bowed wafers may be influenced by the wafer size for larger areas. For the *in situ* measurements this can be neglected because of the only small curvature values obtained under these conditions.

3. Strain and Bow of Grown Layers

Owing to the difference in the thermal expansion coefficients between GaN and sapphire and the resulting stress, GaN layers still connected to a 430 µm thick sapphire wafer show a strong convex bowing at room temperature. Starting with the simplest assumption that they are flat during growth, we have determined the expected strain and bow at room temperature following an approach published by Etzkorn and Clarke [8]. The elastic coefficients needed in these calculations have been taken from [9], whereas the thermal expansion coefficients were taken from [10].

Figure 1 shows the in-plane strain (left axis) and stress (right axis) at the layer surface as well as at the substrate-layer interface expected at room temperature in such bowed samples. Data measured by PL on GaN layers still connected to the sapphire substrate coincide quite well to the surface values.

The curvature expected under those assumptions is plotted as a function of the layer thickness in Fig. 2. However, the curvature measured at room temperature by x-ray diffraction on the same samples deviates significantly from these data. In order to solve this problem, we have measured the curvature of such samples and its development *in*

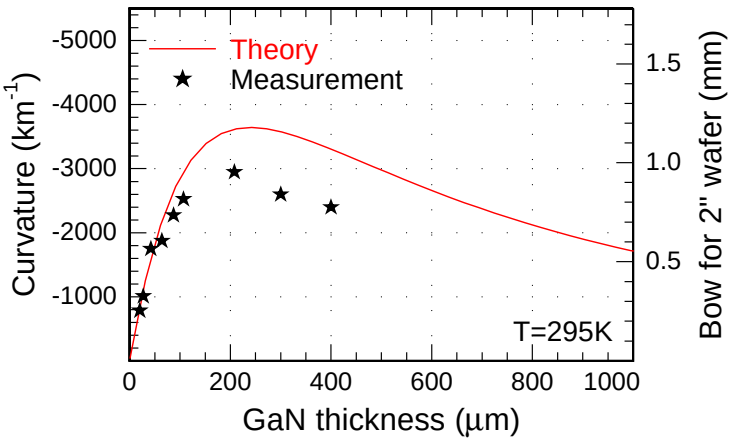

Fig. 2: Wafer bow at room temperature (full red line) determined from the calculated strain data (Fig. 1) as compared to data measured by x-ray diffraction (black stars).

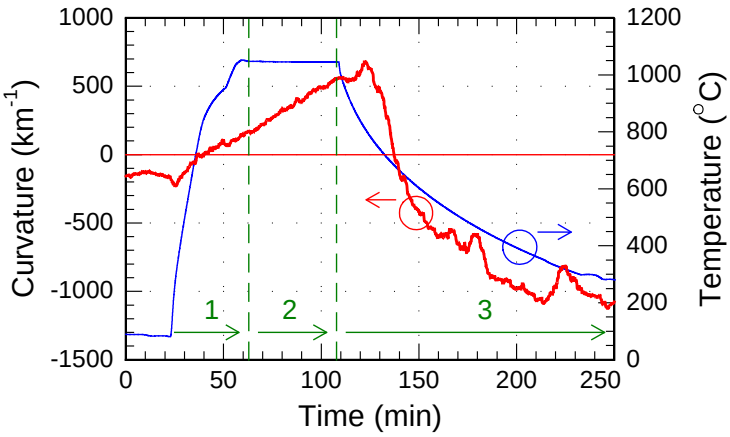

Fig. 3: Development of curvature measured *in situ* during the HVPE run (red line). The blue line shows the temperature profile during the growth process: Phase 1: Heatup; Phase 2: Growth; Phase 3: Cool-down.

situ during the HVPE growth (Fig. 3). For the beginning of the growth process where such measurements can be obtained (see section 2.), we typically find a linear increase of the curvature with a slope of about $6.8\,\mathrm{km}^{-1}/\mu\mathrm{m}$, i.e. the wafer does not stay flat during growth. As shown in Fig. 4, the *in situ* measured curvature (green squares) fits well to the difference of the *ex situ* measured curvature to the expected values depicted in Fig. 2 (brown circles). It can be explained by an in-plane strain of about $5 \cdot 10^{-4}$ (full blue line), already being present during growth. Obviously, it is then frozen in the samples and hence determines the curvature of the GaN layer after separation from the sapphire wafer.

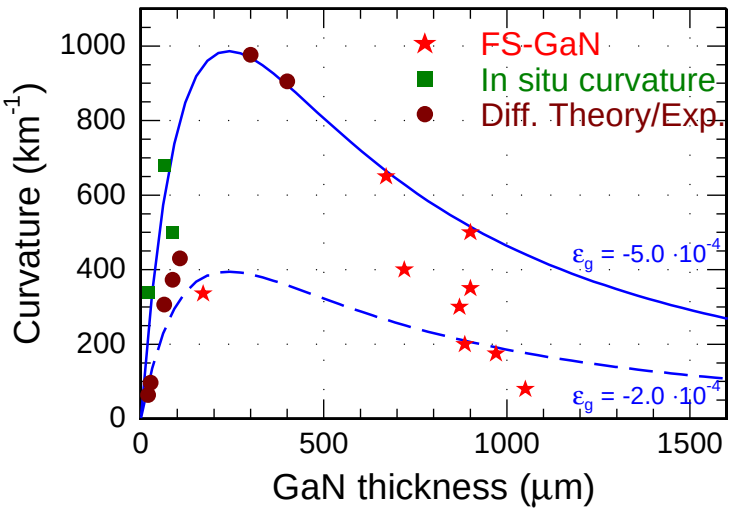

Fig. 4: Curvature of GaN layers measured *in situ* during HVPE growth (green squares) and difference of the *ex situ* measured curvature to the expected values depicted in Fig. 2 (brown circles) versus layer thickness. The full and broken blue lines show the curvatures which are expected for a tensile in-plane strain of about $5 \cdot 10^{-4}$ and $2 \cdot 10^{-4}$ of the GaN layer, respectively. The red stars show *ex situ* measured curvature data of free-standing wafers.

4. Bow of Free-Standing GaN

Normally, such strain results from different lattice constants on the top and the back side of the sample, which in many cases is caused by different thermal expansion coefficients of the two materials of a bi-layer system as discussed above. However, it is not clear what could make such differences in free-standing GaN which is expected to be fairly homogeneous through-out. Indeed, we found that the curvature, once established, does not change between room temperature and 1000 °C (Fig. 5) ruling out any gradients of the thermal expansion coefficient over the wafer thickness. Moreover, it shows that the wafer bow and the responsible strain cannot be easily annealed even after the sapphire wafer is removed which is regarded as the primary cause of any built-in strain.

What else could be responsible for this built-in strain? Free-standing GaN grown by HVPE typically contains a strong gradient of defect density. At the beginning of growth, the layer starts with a dislocation density in the range of at least $10^8\,\mathrm{cm}^{-2}$ to $10^9\,\mathrm{cm}^{-2}$ as a consequence of the hetero-epitaxy on sapphire. As already mentioned, this number decreases steadily during growth by defect annihilation [2] ending somewhere below $10^6\,\mathrm{cm}^{-2}$ for mm-thick layers [3]. In order to study the influence of this dislocation density gradient on the strain and bow of our free-standing GaN samples, we have removed the back-side by etching with molten KOH at 360 °C. This etchant only attacks the N-face, hence the back-side of the GaN layers, whereas the front Ga-face remains fairly unetched. This chemical etching should not have any direct influence on the bowing in contrast to mechanical polishing. Indeed, the curvature can be decreased by this procedure (Fig. 6, left). We found a linear behaviour between the change in curvature and the removed layer thickness. However, even when extrapolating these lines to the complete removal of the

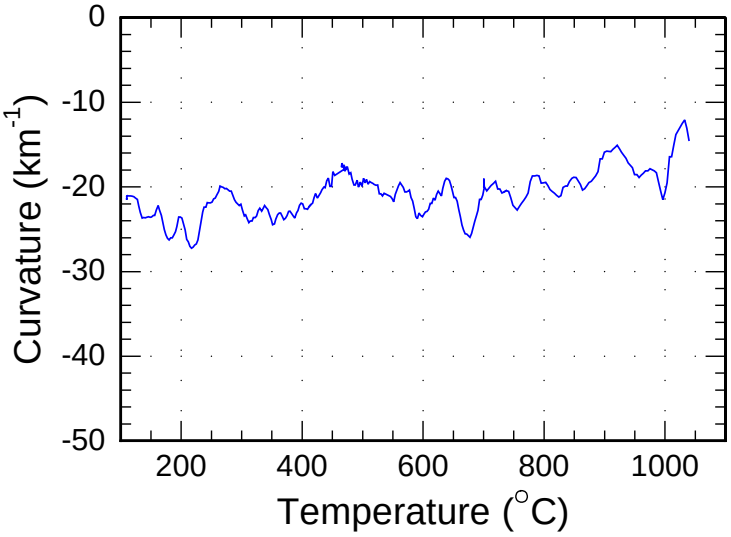

Fig. 5: Curvature of a free-standing GaN sample versus temperature. Notice that the curvature value is quite low because we have polished flat the surface of this particular sample to apply our optical *in situ* curvature measurement.

layers, still a significant bowing remains. Surprisingly, we find for many different samples that about 60 % of the bowing survives for such a complete etching (Fig. 6, right), although the absolute values fluctuate in some range (c.f. Fig. 4). Similarly, Chen et al. [11] found a linear decrease of the curvature after inductively plasma etching of free-standing GaN samples from initially 670 km^{-1} to zero and eventually to convex bowing. We currently can only speculate why their results are quite different to ours taking into consideration the differences in the details of the epitaxial processes and/or the influence of the dry-etch procedure on the wafer bow.

These results indicate that the dislocation density gradient is only partly responsible for the wafer bow of free-standing GaN. We should, however, notice, that the defect density declines inversely proportional to the thickness [2], whereas we found a proportional decrease of the curvature. Moreover, the different curvature values of the unetched samples (see Fig. 6, left) need to be explained. This fact may be related to different strain situations initiated in the very beginning of the growth or even in the MOVPE template. As reported by several groups, in many cases, MOVPE grown layers are fairly weakly strained at room temperature which translates into a significant tensile strain at growth temperature. Such tensile strain is explained to be caused by the coalescence of crystalline islands during nucleation [12] and depends on the details of the nucleation process (see, e.g., [5, 13]). More studies of the correlations between the MOVPE template strain and the curvature of free-standing HVPE-grown layers are currently underway in our labs and will be reported elsewhere.

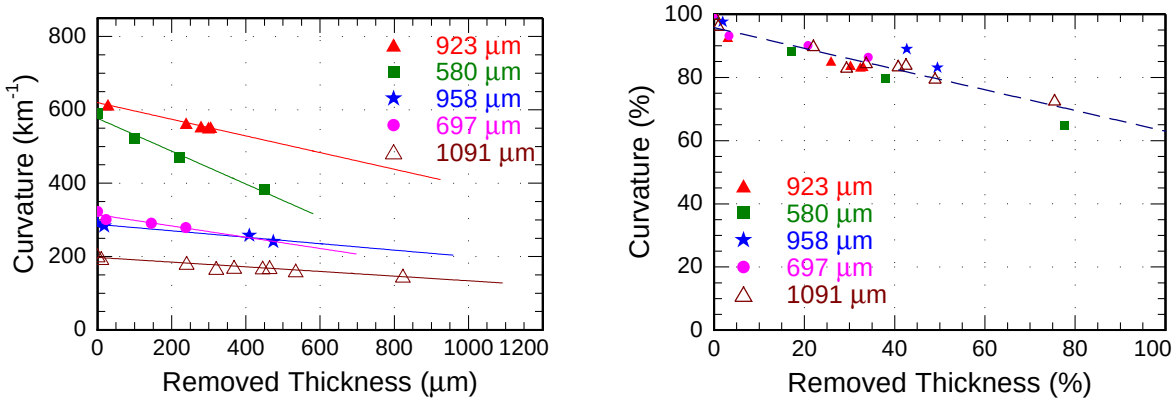

Fig. 6: Left: Curvature of free-standing GaN samples with various thicknesses as indicated in the legend measured by x-ray diffraction after several steps of KOH etching. Right: Same data with thickness axis normalized to the total original thickness of each sample and curvature axis normalized to the value of the unetched samples.

5. Summary

Thick GaN layers grown by HVPE typically are considerably bowed concavely. By comparing *in situ* curvature measurements to *ex situ* curvature and strain evaluations, we could show that this bow is already present during growth and then frozen in the layers, although the different thermal expansion coefficients of GaN and sapphire may lead to strong intermediate convex bow during cool-down of the samples. Some inherent strain developing in the very beginning of the epitaxial growth or even in the MOVPE-grown template may be responsible for it. However, we could not yet determine a cause for the strain still being present in the GaN layers after removal of the sapphire substrate. The dislocation density gradient from the back to the front side can only partly explain our observations.

Acknowledgment

The assistance of Martin Klein, Xiang Yao, (Inst. of Optoelectronics), Joachim Wiest, Benjamin Neuschl, Klaus Thonke (Inst. of Quantum Matter, Semiconductor Physics Group, Ulm University) and K. Koyama et al. (Namiki Precision Jewel Co. Ltd., Japan) is gratefully acknowledged. This work has been financially supported by the Bundesministerium für Bildung und Forschung (BMBF) and by Freiberger Compound Materials GmbH, Freiberg, Germany.

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