Investigations of an In-situ Etching Technique of a Sacrificial ZnO Buffer Layer for the Fabrication of Freestanding GaN in Hydride Vapor Phase Epitaxy

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By in-situ etching of a ZnO buffer layer freestanding GaN layers were prepared by hydride vapor phase epitaxy (HVPE). For the template growth, single crystalline ZnO buffer layers, grown by pulsed laser deposition on sapphire, were used. They were overgrown with a thin GaN layer by a multilayer growth using metal organic vapor phase epitaxy (MOVPE). The removal of the ZnO buffer during the HVPE growth allowed the fabrication of strain-free freestanding GaN layers with a full width-half-maximum of the donor bound exciton ($\mathrm{D^0X}$) *of 2.3 meV at a position of 3.47 eV in low temperature (15 K) photoluminescence.*

1. Introduction

Unlike other established semiconductor material systems, nowadays GaN technology is based on heteroepitaxy on foreign materials due to missing GaN-substrates. For the fabrication of these demanded substrates, the hydride vapor phase epitaxy (HVPE) is considered as the most promising tool. Nevertheless HVPE growth of GaN is still a heteroepitaxial process, requiring a removal technique of the used substrate from the grown GaN layer. Many approaches towards that challenge were reported in the literature, such as laser-lift-off (LLO) [1], mechanical polishing for substrate removal [2], or growth on etchable substrates. Also good results could be achieved by the use of inserted cavernous interlayers which work as breaking points during cool-down from the growth temperature of about 1050°C [3].

Because the substrate removal is done afterwards, the growth is always carried out under strained conditions due to the lattice mismatch. Additional stress arises from different thermal expansion coefficients of GaN and the substrate while cooling down the sample. Together with the stress introduced by the separation method, this leads to a damage of the GaN layer and also can lead to a high dislocation density and strong bowing depending on the separation method. Also the GaN wafers often break during the substrate removal due to the induced high stress.

In this work we investigate an in-situ separation technique during HVPE growth that allows to avoid thermal stress during cool-down introduced by the mismatch of thermal expansion coefficients and also allows to do the growth on a strain-free quasi-substrate [4]. Therefore, we use a sacrificial interlayer made of ZnO that can be easily etched in the HVPE process. Because of its similar material properties compared to GaN, ZnO is the ideal candidate for that purpose. Especially the small lattice mismatch of only about 1.9%

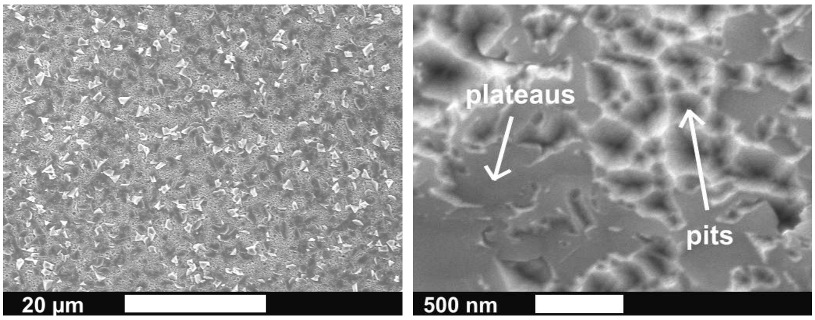

Fig. 1: SEM images of the template surface with several small crystallites (left). In higher magnification (right) a large number of pits and formed plateaus are visible.

and the fact that ZnO can be easily etched makes it very attractive. However, the extreme instability of ZnO in the HVPE atmosphere demands a protecting cover layer of GaN before growth. While other groups have successfully deposited GaN on ZnO by molecular beam epitaxy [5], we employ metal organic vapor phase epitaxy (MOVPE) as commonly used in GaN technology. The created templates can be successfully overgrown by HVPE and the ZnO buffer is removed in-situ, resulting in a free standing quasi substrate avoiding any strain from a lattice-mismatch or stress during cool-down due to a difference in thermal expansion coefficients.

2. Experimental

The templates prepared for the HVPE growth consisted of an approx. 600 nm thick ZnO layer on sapphire, grown by pulsed laser deposition as described elsewhere [6]. The samples were subsequently overgrown with a thin GaN cover layer by a multistep procedure in an AIXTRON AIX 200 RF low pressure (LP)-MOVPE system by using trimethylgallium (TMGa) and NH_3 as precursors. First, a low temperature cover layer was grown at fairly low temperature of 550°C using N_2 as carrier gas in order to protect ZnO from etching at the onset of the growth process. Afterwards, an intermediate layer at 800°C was grown to minimize the diffusion of Zn and O_2 into the finally grown top layer which was deposited at a temperature of 900°C. For this final layer and the intermediate layer H_2 and N_2 were used as carrier gas. In between these layers, different annealing steps were performed, while the pressure was kept constant at 100 mbar during the complete MOVPE process [7].

The HVPE growth was performed in a commercial Aixtron single-wafer HVPE system with a horizontal quartz-tube, heated in a furnace with five zones. Nitrogen and hydrogen were used as carrier gas. As nitrogen precursor, ammonia was applied, while for the group-III element GaCl was used, formed inside the reactor by streaming HCl-gas over a liquid Ga source heated to 850°C. For the growth a three step procedure was developed. The goal of the first step was the formation of a GaN layer, stable enough that it can act as a freestanding quasi substrate for the subsequent growth after the in-situ lift-off. In this step dissolving of the ZnO must be prevented before the GaN-layer is stable enough.

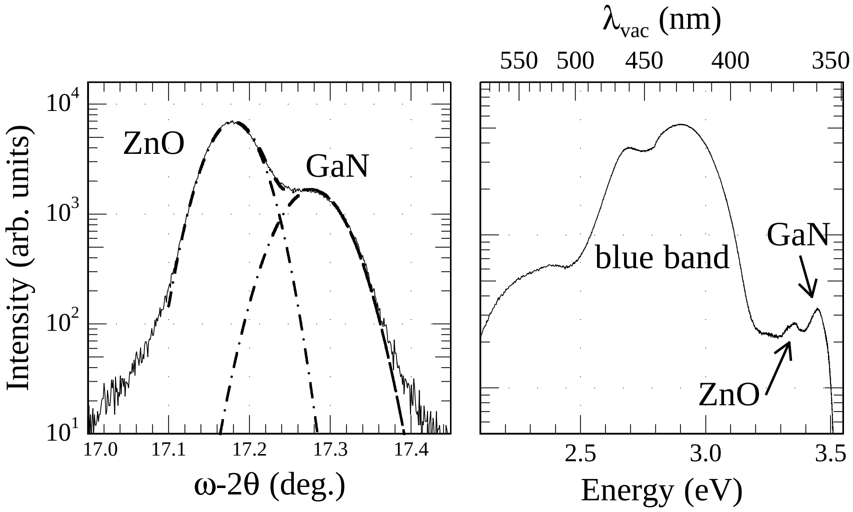

Fig. 2: MOVPE grown template: ω-2θ-scan of (0002)-reflection of HRXRD measurement (left). GaN and ZnO peak can clearly be distinguished. In the LT-PL spectrum (15 K) ZnO and GaN-peaks are visible (right).

In a second step, the etching of the sacrificial ZnO buffer was performed, while the growth rate was drastically decreased or even stopped. By increasing the hydrogen concentration of the carrier gas while slowly increasing temperature, the ZnO was completely etched. This is the most critical part of the process, since high temperature is inevitable to accelerate the etching, but is precarious as it introduces thermal stress to the sample because the thermal expansion coefficients of sapphire, ZnO and GaN are strongly different [1]. Finally a separated free-standing GaN layer is prepared for the final high-temperature growth.

After the lift-off, a thick high-temperature (HT) layer of several hundred µm was grown in the last step at optimized growth conditions [8]. Therefore, a temperature of 1050°C and a pressure of 900 mbar were chosen and the growth rate was adjusted to be about 150 µm/h.

Scanning electron microscopy (SEM) and high resolution X-ray diffraction (HRXRD) measurements were carried out to investigate surface morphology and crystal quality. The optical properties were investigated by low temperature (15 K) photoluminescence (PL) and high resolution cathodoluminescence (CL) spectroscopy.

3. Results and Discussion

3.1 MOVPE growth

The total thickness of the GaN layer grown in MOVPE was approximately 600 nm. The samples showed a light yellow color and on the surface still many pits and defects could be detected. However, the emergence of large areas of plateau-like flat surface indicates the 2D-growth of GaN. Figure 1 shows SEM pictures of the surface. The formation of

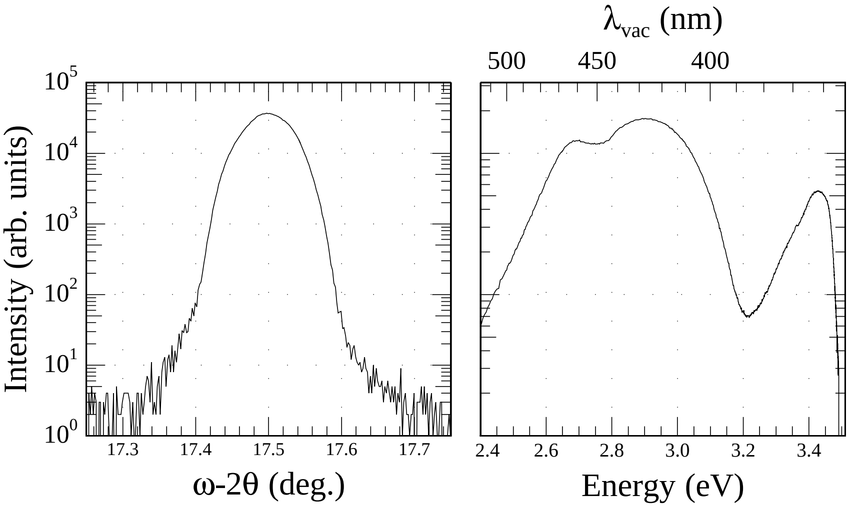

Fig. 3: The ω-2θ scan of (0002)-reflection in HRXRD- (left) and the LT-PL- (right) measurement shows the comparably low quality of the grown LT-layer in the first HVPE step. Compared to the used template, the GaN peak shows a drastically increased intensity.

small crystallites on the surface could not be completely avoided, but the density could be reduced to less than $10^7\,\mathrm{cm}^{-2}$.

The quality of the GaN layer was investigated by PL and HRXRD measurements. In the LT-PL spectrum (Fig. 2) a clear signal from the GaN at 3.44 eV could be detected, as well as a peak related to ZnO at 3.34 eV. The broad luminescence band at around 2.9 eV is typical for Zn doped GaN [9], probably a result of gas phase diffusion during growth. Also in Fig. 2 a ω-2θ-scan of the (0002)-reflection is shown. The two peaks related to ZnO and GaN can be clearly distinguished, confirming the well-ordered c-plane crystalline growth of the GaN layer on the ZnO film. More details can be found elsewhere [7, 10].

3.2 HVPE growth

In the first HVPE step, an approximately 50 µm thick GaN layer was deposited. The choice of growth parameters for this step is demanding, because etching of the ZnO must be reduced to a minimum, until a stable GaN layer is achieved. We found, that at temperatures above 900°C the ZnO layer is already completely dissolved during this first step. The ZnO is also etched, if hydrogen is present in the reactor during this LT growth. At 900°C and without H_2 in the carrier gas, a closed uncracked GaN layer of 50 µm thickness could be grown on the ZnO-GaN template. The quality of this layer is still comparably low due to the low growth temperature. So HRXRD measurements showed a full width at half maximum (FWHM) of the (0002)-reflection of about 1400 arcsec, and the PL-spectrum is still dominated by the blue luminescence band around 2.9 eV (Fig. 3). Moreover the surface is very rough after this step (Fig. 4).

After the LT layer, the growth is interrupted and the temperature is increased to 950°C to achieve a stronger dissolution of the ZnO. The moderate temperature ramp was necessary,

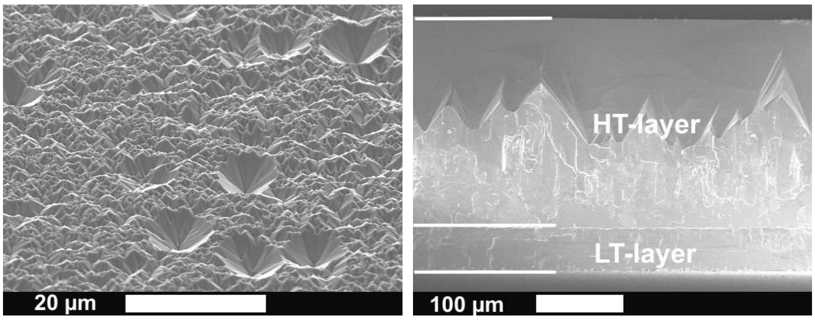

Fig. 4: The SEM picture of the LT HVPE layer shows a very rough surface (left). In the cross-section (right) the LT layer can be clearly identified. The strong contrast in the SEM picture is probably attributed to ZnO incorporation.

otherwise the ZnO dissolved too fast, resulting in many holes and cracks of the GaN layer. By adding hydrogen to the carrier gas and increasing the ammonia flow, the etching of the ZnO, starting at the sample edges, is encouraged. It also causes the formation of channels to allow the dissolved ZnO to escape (Fig. 5). The LT layer is separated from the sapphire during this step, remaining as a freestanding quasi substrate on top of the sapphire.

Finally, the temperature is further increased to 1050°C for the growth of an approximately 250 µm thick HT-layer of higher quality. Obviously, first a highly defective layer grows, probably due to some disturbance of the low temperature layer having lower quality. Additionally, we suppose that last traces of ZnO are removed during this step leading to high Zn doping which may be responsible for the brownish color of our samples. After about 150 µm growth, an abrupt change of contrast is visible in the cross section SEM picture (Fig. 4) indicating a much lower defect density in the top part of this layer. This abrupt change from defective material to good layer quality may also explain the strong bowing of our samples which has still to be reduced and currently limits their total thickness. Also the areal size of the final samples is currently limited by crack formation to about one cm^2.

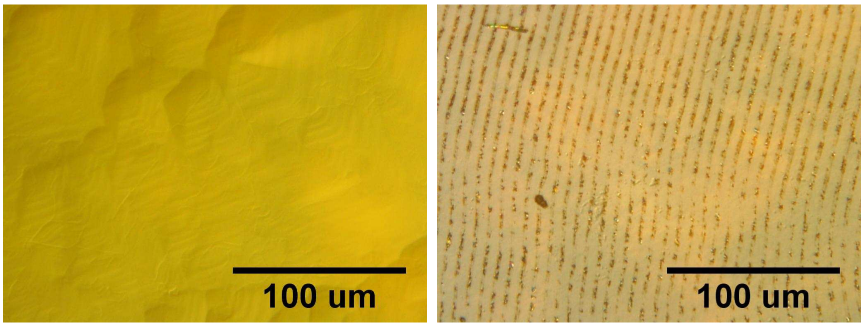

Fig. 5: Optical microscope images of the smooth surface (left) and backside (right) of the final sample. On the backside the formed channels of the dissolving ZnO are clearly visible.

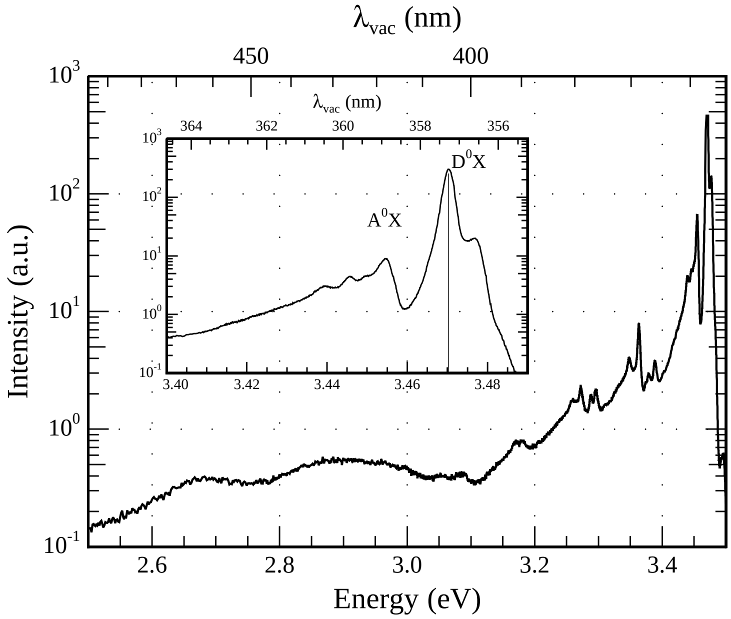

Fig. 6: Photoluminescence spectrum (15K) of the HT-GaN layer (300 μm) on top of the sample. Position of D^{0}X at 3.470 eV indicates a strain-free surface. The spectrum also shows an intense peak of an acceptor-bound-exciton at 3.455 eV related to Zn-incorporation. Strong phonon replica of both peaks are visible.

By low temperature (7 K) CL measurement along the cross-section (Fig. 7) we analyzed the strain situation in the samples. The first 50μm of the LT layer were grown under tensile strain due to the lattice mismatch of GaN and ZnO, what could be responsible for a shift to lower energies of the D^{0}X. Only the lowest regions were relaxed by the formation of some micro-cracks. After the removal of the ZnO-buffer the first HT-GaN layers were grown under compressive strain, due to the concave bowing of the sample. With increasing thickness and less incorporation of Zn, the top layers are more and more strain free.

A low-temperature (15 K) PL-spectrum of the top of the final free-standing sample with about 300 μm HT-GaN is shown in Fig. 6. The position of the donor bound exciton (D^{0}X) at 3.470 eV indicates a strain-free surface. The FWHM of 2.3 meV for the D^{0}X is still high compared to GaN on sapphire, but very narrow for GaN on ZnO. Beside the D^{0}X, a strong peak of an acceptor-bound exciton at 3.455 eV with strong phonon replica can be found and is related to Zn doping. A localization energy of 22 meV with respect to the free A exciton at 3.477 eV was obtained for this A^{0}X.

4. Summary

We successfully have overgrown a ZnO-buffer layer with GaN by MOVPE and a subsequent HVPE step. The fabrication of freestanding GaN by an in-situ etching technique in HVPE could be realised, while the lift-off occured already during growth. Unfortunately,

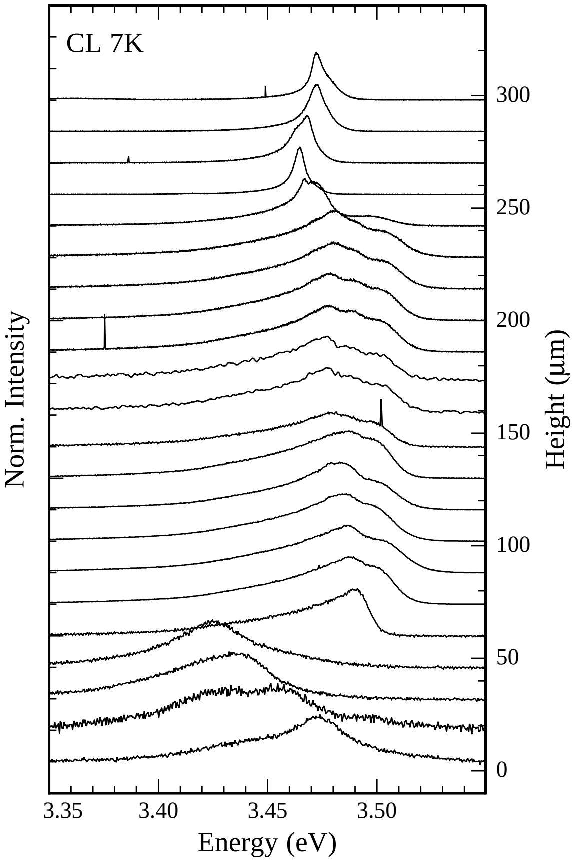

Fig. 7: Low temperature (7K) CL-measurement of the cross-section of the final sample. The first 50µm were grown at low temperature on the ZnO-GaN-template, resulting in a tensile strain. After the removal of the ZnO the first GaN-layers are compressively strained, until a unstrained situation is achieved on the top.

the poor quality of the low temperature layer results in high defect densities also in the overgrown HT-layer. However, the avoidance of stress arising from different thermal expansion coefficients during cool-down or due to a lattice mismatch of GaN and substrate makes the technique anyway very promising for future production of GaN substrates.

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