

Reactor and growth process optimization for growth of thick GaN layers on sapphire substrates by HVPE

E. Richter^{a,*}, Ch. Hennig^a, M. Weyers^a, F. Habel^b, J.-D. Tsay^{b,1}, W.-Y. Liu^{b,1}, P. Brückner^b, F. Scholz^b, Yu. Makarov^c, A. Segal^c, J. Kaeppler^d

^a*Ferdinand-Braun-Institut fuer Hoechstfrequenztechnik, Materials Technology, Gustav-Kirchhoffstr. 4, 12489 Berlin, Germany*

^b*Optoelectronics Department, University of Ulm, 89081 Ulm, Germany*

^c*STR Inc. P.O. Box 70604, Richmond, VA 23255, USA*

^d*Aixtron AG, 52072 Aachen, Germany*

Abstract

In total, 120 μm thick GaN layers without cracks have been grown on 2 in sapphire substrates by hydride vapor phase epitaxy. This has been achieved by optimization of the flow patterns in the reactor based on 3D process modelling, choice of the growth parameters especially the carrier gas composition and the usage of suitable GaN/sapphire templates. An important finding is that an H_2 content of around 50% in the N_2 carrier yields the lowest crack density.

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1. Introduction

In recent years, GaN and related ternary compounds have found a tremendous attention due to their excellent properties for short wave-

length optoelectronics and high-power high-frequency electronics. Device structures are epitaxially grown on foreign substrates mostly like sapphire or SiC by means of MOVPE or MBE. The hetero-epitaxial growth on foreign substrates is responsible for a large defect density, limiting drastically the properties of the more advanced devices like short wavelength laser diodes. These problems could be overcome by using GaN substrates. However, up to now there is no way

*Corresponding author. Tel.: +49 (0)30 6392 2704; fax: +49 (0)30 6392 2685.

E-mail address: richter@fbh-berlin.de (E. Richter).

¹On leave from ITRI, Hsinchu, Taiwan.

of producing such substrates by the conventional way of crystal growth primarily due to the limited nitrogen solubility and diffusion in liquid gallium [1].

Currently, the most promising way out is the hetero-epitaxial growth of thick GaN layers by hydride vapor phase epitaxy (HVPE), which is studied by several groups [2–5].

However, also in HVPE the growth starts on a foreign substrate and the resulting difficulties have to be studied. One of these consists in the formation of cracks that appear when a critical thickness is exceeded, e.g. on sapphire already after the growth of only a few micrometers of GaN. In early investigations evidence was found for the formation of microcracks in the sapphire substrate during the GaN growth, but the formation of macrocracks which extend to the GaN surface was assumed to originate from the thermal mismatch only [6]. Later when layer growth exceeded 100 μm it was found that effective relaxation processes exist [7]. The growth of crack-free GaN substrates with diameter of nearly two inch has been demonstrated [2]. The commercial availability is still very limited demonstrating that still no simple and reliable process could be established. It was found that cracks are usually formed already during growth due to tensile strain, which builds up from the early nucleation process [8]. This early crack formation can have a detrimental effect because microcracks into the sapphire substrate may serve as initial breaking points afterwards for the relief of increasing strain due to the different thermal expansion coefficients of the layer and the substrate during cool-down [8]. This holds even when growth conditions can be found that result in healing of the cracks during growth. The diffusivity of growth species on the surface has been assumed to be an important parameter for this crack healing.

In this study, we demonstrate that thick, crack-free GaN layer growth can be achieved when the reactor design allows for stable, well defined growth conditions, appropriate GaN layers on sapphire are used for the growth start and the carrier gas composition is optimized for minimized strain incorporation during the growth process.

2. Experimental

Growth experiments have been performed in Aixtron AIX-HVPE horizontal quartz reactors.

The reaction chamber is a quartz tube that is heated in a furnace with five zones. Nitrogen or N_2/H_2 mixtures are used as the carrier gas injected in zone 1 (Fig. 1a). The group III source of liquid Ga is placed in zone 2 in one of two inner quartz tubes in the upper part of the reactor. GaCl is formed at elevated temperatures of 850–950 °C from HCl and is injected via a tilted shower head above the substrate. The second quartz tube is a counterpart purged with nitrogen. An NH_3/N_2 mixture is introduced via a separate quartz tube with a nozzle in zone 3 just before the substrate holder. The rotating substrate is placed in zone 4. Growth results using this type of reactor have already been published, e.g. for direct growth on sapphire [9] and for GaN layer growth on structured templates [10].

Flow patterns for this geometry have been investigated in comparison of experiments and simulations.

Experimental visualization of flow patterns was found to be possible due to the immediate formation of ammonium chloride (NH_4Cl) powder when gaseous hydrogen chloride and ammonia meet at room temperature.

Stream lines of the group V gas flow have been observed when ammonia enters via the nozzle in zone 3 into the reactor with small amounts of hydrogen chloride continuously added to the nitrogen carrier gas in zone 1. Stream lines of the group III gas flow have been observed when hydrogen chloride enters the reactor via the shower head into a continuous gas flow containing ammonia. In the latter case, the powder contamination was found at similar positions where GaN growth takes place at high temperatures either as intended on the substrate or as non-intended parasitic depositions on quartz parts. The ammonium chloride contaminations can easily be removed by heating the system above 350 °C.

Self-consistent 3D computer simulations of the species transport have been performed including heat and radiation transfer, flow dynamics, species diffusion, and surface chemistry for the parameter

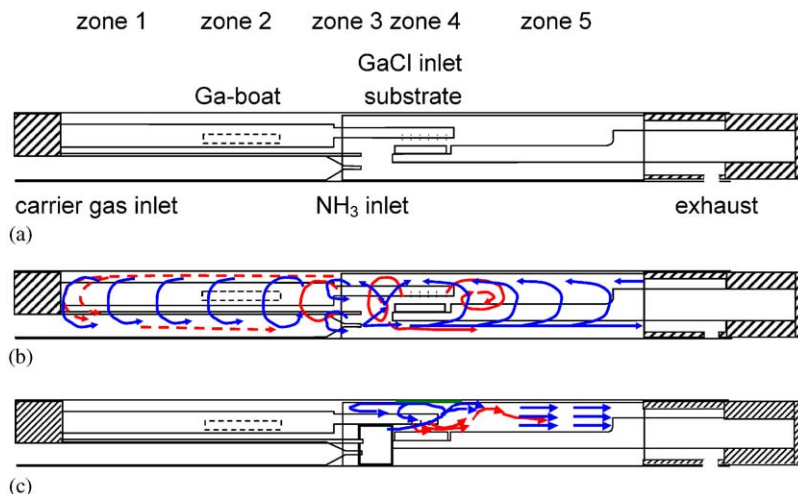


Fig. 1. Reactor geometry (a), flow pattern at 950 hPa with original reactor geometry (b) and flow pattern with the new gas regulation chamber which redirects the ammonia directly onto the substrate (c) as observed by the formation of ammonia chloride at room temperature. The carrier gas flow rate in (c) is increased to 9 l/min of nitrogen for 950 hPa to avoid a standing vortex above the substrate. Group V flow with NH_3/N_2 mixture (blue), group III flow with HCl/N_2 mixture (red), carrier gas is pure nitrogen.

sets used in the experiments. The surface kinetics is described in these simulations using a quasi-thermodynamic approach that is adopted to GaN HVPE [11]. According to this approach, species adsorption/desorption are considered as the limiting stages of surface kinetics while the other stages are assumed to proceed under quasi-equilibrium conditions. As applied to GaN HVPE, the approach employs also the assumption that the N_2 sticking probability on GaN is so small that nitrogen is not involved in the surface chemistry. This means, in particular, that NH_3 decomposition into H_2 and N_2 at GaN surface is essentially suppressed by the low nitrogen reactivity. Simultaneously, surface reactivity of the other species is sufficiently high for the growth reaction $\text{GaCl} + \text{NH}_3 \rightarrow \text{GaN(s)} + \text{HCl} + \text{H}_2$ to proceed without kinetic limitations. All these assumptions are confirmed by good agreement of the computed and experimental data reported in Ref. [11].

On the basis of the findings on the flow patterns, hardware changes have been made to yield improved flow patterns with the mixing point of group III and group V species being on the substrate and minimized contact of gases with parasitic deposits before the growth reaction. This was achieved by the introduction of a gas

regulation chamber that redirects the ammonia directly onto the substrate.

Two types of starting GaN layers on 2-in (0001) sapphire templates have been used for subsequent growth of thick GaN layers. Templates grown by MOVPE consist of a $1.5 \mu\text{m}$ thick GaN layer grown on a low-temperature GaN nucleation layer. Templates grown by HVPE were grown for comparison similar to Ref. [9].

For the template layers directly grown by HVPE on sapphire substrates low-temperature GaN nucleation on sapphire and buffer growth was performed at 200 hPa with constant total flow rates in the carrier gas of 6 l/min, in the group V line of 1.5 l/min and in the shower heads of 300 ml/min. Nitridation was performed with a 2:3 mixture of ammonia and hydrogen in the group V line at a substrate temperature of 1045°C for 10 min. The subsequent nucleation layer was grown with a 2:3 mixture of ammonia and nitrogen in the group V line and with 15 ml/min hydrogen chloride diluted in nitrogen in the group III line at 600°C for 11 min. The layer was heated up for re-crystallization to 1000°C for 5 min and GaN growth was performed subsequently. A growth rate of $28 \mu\text{m/h}$ was used at a substrate temperature of 1000°C and a total pressure of 400 hPa with 1:4 mixture of

ammonia and hydrogen in the group V line and unchanged group III supply for the growth of 2–4 μm thick GaN layers.

Thick GaN layers of about 100 μm have been grown on templates grown by MOVPE.

The influence of different growth parameters like nitrogen/hydrogen ratio in the main carrier gas, V–III-ratio, reactor pressure between 200 and 1000 hPa and growth temperature between 1030 and 1075 $^{\circ}\text{C}$ have been studied. The HCl flow rate was kept constant at 20 ml/min for all experiments discussed in this paper.

In order to separate the influence of the not yet completely optimized HVPE nucleation layer and other growth parameters on the characteristics of thick GaN layers, half of each template type was used for the growth of a thick GaN layer with optimized conditions in parallel.

3. Results and discussion

Before starting optimization of growth parameters the suitability of growth hardware to provide reproducible and stable growth conditions was tested. Gas flow patterns at a total pressure of 950 hPa observed experimentally at room temperature for the original reactor geometry and for the improved reactor geometry are shown in Fig. 1b and c.

The ammonia/nitrogen mixture is injected via the nozzle. If there is no barrier, it forms a jet flow below the substrate towards the exhaust region on the right side of the reactor. There it turns up and forms a backflow. The backflow continues until it turns back in a second vortex at the very beginning of the reactor tube. The second vortex can be shifted downstream towards the right side of the Ga source if the total pressure is lowered down to 200 hPa. At all conditions, the group III flow is carried along with the backflow, which results in a shift of the mixing point upstream to the left side of substrate. Computer simulations reproduce the observed non-uniform vortical flow structure and allow associating it with a strong NH_3/N_2 stream coming out from the group V injector. It is known that the thermal decay of ammonia is usually a sluggish reaction [12] but catalytic effects can

accelerate it. It is obvious from the flow patterns that the reactive species may turn in a circle and the gas composition may change with the growth of parasitic GaN deposits at the reactor walls. Indeed, we found that the backflow pattern affected the run-to-run reproducibility of surface morphologies and growth rates tremendously.

In contrast, the gas regulation chamber (Fig. 1c) builds not only a barrier for the ammonia/nitrogen mixture but forces the flow via a wide slit onto the substrate with a moderate velocity of about 3 cm/s. Simulations of flow pattern with the same sets of flow parameters but using actual growth temperatures provided coincidence with the experimental findings. The corresponding distributions of molar fractions of ammonia and gallium chloride for this case are shown in Fig. 2a and b for 950 hPa. It is seen that NH_3 coming out from the wide slit located somewhat upstream and above the susceptor is uniformly distributed over the wafer. GaCl is distinctly shifted downstream by the ammonia flow, however, this non-uniformity is essentially smoothed by the wafer rotation. No

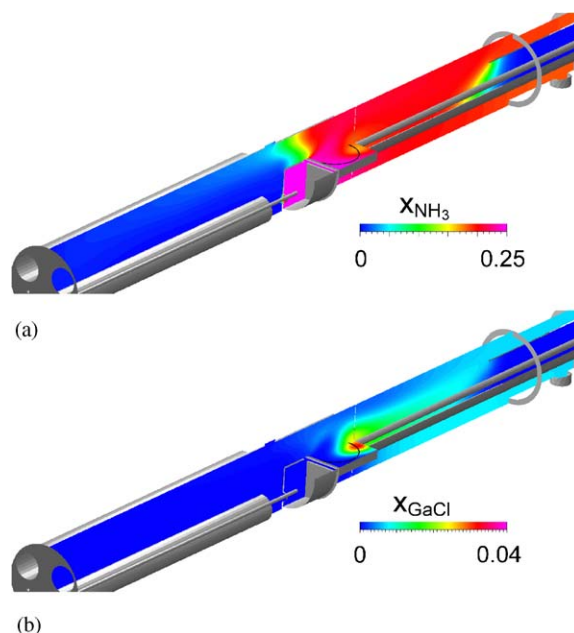


Fig. 2. Process modelling results for reactor with gas regulation chamber at 950 hPa and $T = 1050$ $^{\circ}\text{C}$. Distribution of the molar fraction of ammonia (a) and the molar fraction of gallium chloride (b) calculated for growth temperature.

remarkable change has to be noted when the total pressure is reduced to 200 hPa. It is worthwhile to note that the Ga mole fraction on the substrate surface increases by a factor of five due to the insertion of the gas regulation chamber with comparable ammonia molar fraction, which allows for more efficient growth. The mixing point is still at the right edge of the substrate susceptor but can be moved to the center by slight modifications of the shower heads. Parasitic deposits are found around the substrate and at the downstream surfaces where the reactor wall is protected with a liner tube.

The observations indicate that experimental results of flow patterns obtained at room temperature are very similar to the flow patterns at growth temperature. The flow patterns are obviously dominated by forced gas convection and natural concentration gas convection due to different densities of the gases involved, whereas temperature induced effects play a minor role. Thus, direct flow pattern observation has been used successfully to modify the reactor hardware and stable growth conditions could be established.

Before installation of the gas regulation chamber, fair GaN layer quality for thicknesses up to about 20 μm had been obtained on MOVPE grown templates when using only nitrogen as carrier gas. These properties could not be recovered after installing the gas regulation chamber even after appropriate adjustment of all gas flows, i.e. all grown layers suffered from strong cracking. However, when hydrogen was mixed to the main carrier gas the GaN layer properties changed dramatically. The growth rate decreases with increasing H_2/N_2 ratio (Fig. 3) since the growth GaN-formation reaction via $\text{GaCl} + \text{NH}_3 \rightarrow \text{GaN(s)} + \text{HCl} + \text{H}_2$ is suppressed by a higher hydrogen concentration, which is simultaneously the carrier gas and a product of this reaction. The surface morphology improved up to an H_2/N_2 ratio of 1:1 for layers with the same final thickness. More importantly, the crack density decreased reaching crack-free layers for this carrier gas composition. When the hydrogen content was further increased, crack formation was again observed as well as an increased surface roughness.

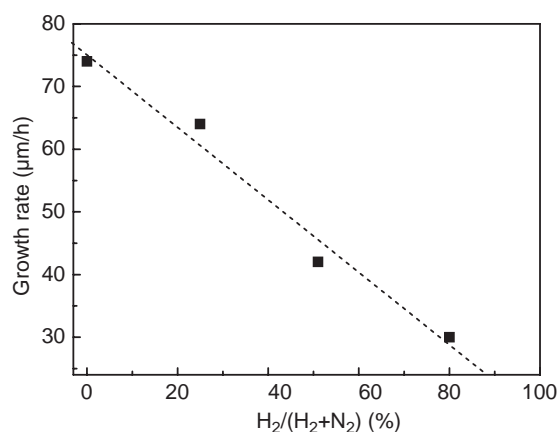


Fig. 3. Growth rate vs. hydrogen content in main carrier gas.

Other important growth parameters are the V/III ratio and the total reactor pressure. Reduction of these parameters was observed to lead to lower growth rates but the layer quality could not be further improved. Thus, we concentrated our further studies on a V/III ratio of 45 and a total reactor pressure above 500 hPa.

By increasing the growth time under these optimized conditions (H_2/N_2 ratio of 1:1), crack-free layers with a final thickness of about 120 μm (Fig. 4) have been obtained. These layers are compressively strained at room temperature as indicated by the bending of the wafers. The strain near the sample surface ϵ_{zz} was estimated to be about of +0.037% from the peak position of the donor bound exciton measured by low-temperature photoluminescence [13]. High-resolution X-ray diffraction showed a quite small line width of the GaN layer of about 115 arcsec. These measurements have been obtained in open-detector mode with an incident X-ray beam diameter of about 50 μm to compensate for the wafer bending. Hall effect measurements on these wafers showed excellent electrical properties with mobilities of about 720 cm^2/Vs for a carrier concentration of $7 \times 10^{15} \text{cm}^{-3}$ which was also obtained by CV profiling [14].

It is worthwhile to note that no cracks could be observed within the GaN layer by means of optical microscopy. Usually, it is described [6,7] that cracks always occur when growth exceeds 4–20 μm and can be still observed in optical microscopy by

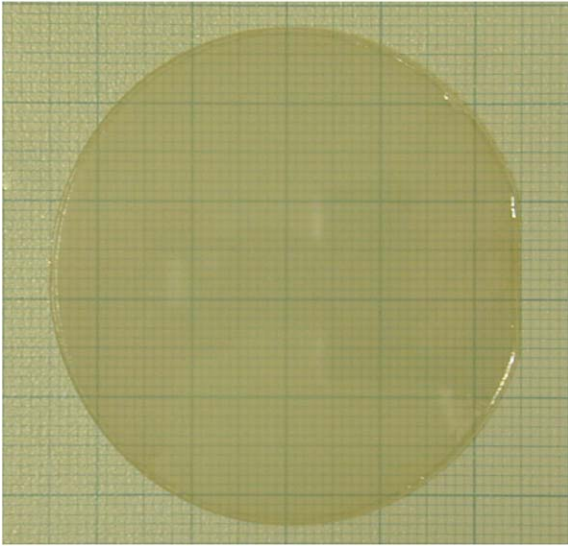


Fig. 4. Photo of a 2 in GaN layer on sapphire with 120 μm thickness without cracks.

moving the focus even after successful healing in much thicker GaN layers [8]. Although it is beyond the scope of this work to analyze the MOVPE nucleation procedure used here in detail, it is suspected that some still unknown property of the GaN/sapphire template can be responsible for the finding that cracks can be avoided on particular template structures.

In order to separate the influence of growth conditions and starting layers, the optimized HVPE growth process was applied on HVPE grown GaN/sapphire templates as well as on the MOVPE grown templates in parallel.

Templates obtained from direct HVPE growth on sapphire were crack-free and specular with a root mean square surface roughness of about 2 nm for $10 \times 10 \mu\text{m}^2$ area scan for a 4 μm thick GaN layer. The large FWHM at the (0002)-reflex of omega-rocking curves of about 600 arcsec indicates that the nucleation process is not optimized yet. The strain near the sample surface ε_{zz} measured by photoluminescence was found slightly tensile with -0.009% for a GaN layer of 4 μm thickness on a 330 μm thick (0001) sapphire substrate.

In case of these HVPE templates serious cracking of the thick layer occurred (Fig. 5a)

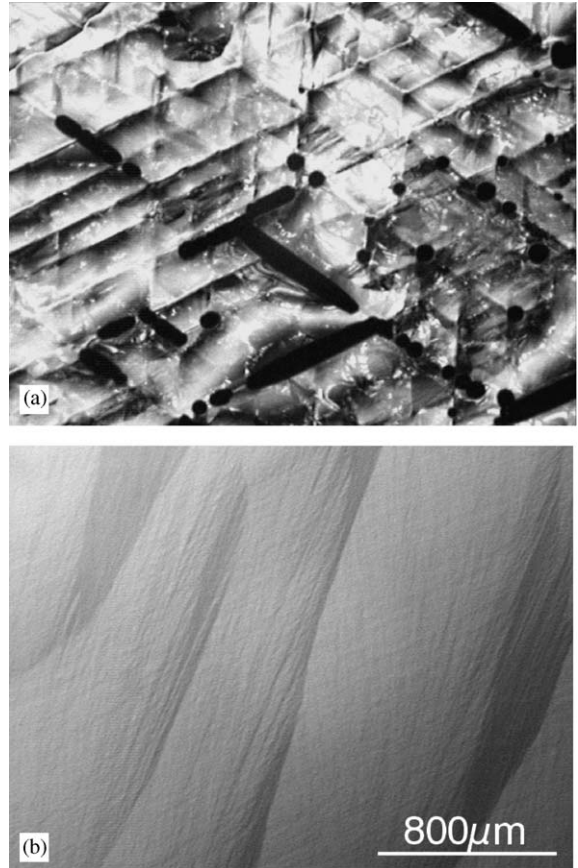


Fig. 5. Optical micrographs of the surface morphology of layers grown in parallel on HVPE-grown templates (a) and MOVPE grown templates (b). Severe cracking is observed on the HVPE-grown template while on the MOVPE-grown one no cracks are visible and a very smooth surface morphology is obtained.

whereas the HVPE layer grown on a MOVPE template showed excellent surface morphology without any cracks (Fig. 5b) although both have been grown in the same epitaxial run.

The properties, which are responsible for the superior behavior of these particular MOVPE grown templates in comparison to the HVPE templates and others [8] when overgrown with a thick GaN layer are still under investigation. Most probably these properties are already a result of growth conditions used for the nucleation layer. Our results demonstrate that finding an appropriate starting layer is—in addition to a growth

environment stable over several hundreds micrometers of GaN growth—a prerequisite to the growth of thick crack-free GaN substrate layers.

4. Conclusions

The growth of crack-free GaN layers with thicknesses exceeding 100 μm on (0001) sapphire substrates by HVPE has been demonstrated using optimized growth hardware as well as optimized growth conditions and an appropriate starting template as substrate.

The reactor design found assures long-term stable, well defined and reproducible growth conditions with the mixing point of GaCl and NH_3 on the substrate. It is found that even rather simple experiments at room temperature can be useful for the optimization of reactor design in case of transparent reactor walls because thermal convection was found to be negligible in this type of reactor. Thus, vortices and backflow phenomena can be studied and can be avoided successfully even near atmospheric pressure both. The experimental observations on flow patterns and parasitic deposition agree well with the results of 3D modelling of the flow. This demonstrates that growth modelling has been developed into a powerful tool for reactor and growth parameter optimization. An optimized reactor design is necessary for the growth of thick layers with stationary growth conditions.

Using an optimized mixture of hydrogen and nitrogen it is possible to reduce the formation of cracks. It is assumed that the supply of hydrogen has an impact on the thermodynamic properties at the surface and enhances the overall mobility of the growth species on the surface. In addition, it was found that crack-free thick GaN layers could only be grown on suitable starting layers. Crack formation on the not yet optimized HVPE grown templates occurs already during the growth probably due to the tensile strain incorporated in the starting layer [8]. No formation of cracks was observed using optical microscopy for the growth of thick GaN layers on the MOVPE grown templates used here. However, from the current results it cannot be concluded yet that the strain

status of the starting layer is the only but one property of starting layer that decides about crack formation.

In summary, the use of well-designed reactors, suitable starting layers, and optimized HVPE growth processes are found to be key factors for the production of crack-free or eventually free-standing GaN layers to be used as substrates. The optimization of the processes urgently needs appropriate starting layers like the MOVPE grown GaN/sapphire template used here. Therefore, further investigations to find out an applicable figure of merit to evaluate GaN/sapphire templates with respect to thick layer growth are required.

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