# Growth Investigations of Nitrogen-Polar GaN Nucleation Layer Templates

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*This study aims at achieving highly crystalline and smooth Nitrogen-polar (N-polar) GaN layers deposited on c-plane sapphire by metal organic vapor phase epitaxy (MOVPE). The influence of nitridation, temperature and V/III ratio on the polarity, quality and coalescence of GaN is systematically investigated. It was observed that the initial nitridation of sapphire before GaN growth is critical for achieving N-polar growth and improving the crystal quality. Moreover, higher GaN deposition temperatures (above 1100°C) result in lower coalescence and growth of vertical micro-hexagonal structures with a large degree of N-polarity, while lower temperatures (below 950°C) resulted in a coalesced layer but lower degree of N-polarity and crystal quality. Growth under a low V/III ratio (below 50) at a temperature of 1000°C showed complete coalescence with a layer thickness of 170 nm and a linewidth of 20 meV for the GaN band-edge emission in low temperature photoluminescence, whereas a higher V/III ratio of 1100 resulted in GaN structures separated from one another (lower degree of coalescence). Finally, selectively grown vertical GaN micro-rods on masked nitridated sapphire proved to be exhibiting mainly N-polar crystal orientation.*

## 1. Introduction

Group III-nitrides have a polar asymmetry along the c-axis of their hexagonal wurtzite crystal structure [1]. As confirmed by the larger number of publications, most light emitting diodes, laser diodes, and high electron mobility transistors have been developed on Ga-polar GaN templates. Recently, N-polar GaN films have attracted increasing attention. The flipped spontaneous and piezoelectric polarizations for N-polar GaN films can be a further degree of freedom for the design in various devices. The advantages include higher chemical surface reactivity for sensor applications [2], lower gate leakage current in N-polar GaN/AlGaN/GaN HEMTs [3] as well as enhancement of vertical growth of selectively grown structures on masked substrates [4]. The latter point could be utilized for the realization of well ordered upright GaN nano- and micro-pillars. The initial nitridation of the sapphire substrate and buffer layer growth have been identified as the main differences in polarity of the GaN films [5]. Growth initiation using a thin GaN or AlN layer at lower temperatures have been reported to result in GaN films with Ga polarity [6]. However, if the sapphire substrate is exposed to the N precursor at high temperatures prior to GaN growth leading to the formation of a thin AlN surface layer [5], typically N-polar GaN films result [7]. In this study we investigate the influence of temperature, nitridation and V/III ratio on the polarity, quality and coalescence of thin GaN nucleation layers (around 170 nm) on c-plane sapphire by metal organic vapor phase epitaxy (MOVPE).

## 2. Experimental

A reference layer template identified for our experiments for the systematic variation of growth parameters is described in Table 1. Trimethylgallium (TMGa) and ammonia ($NH_3$) were used for the deposition of GaN layers. Before the growth, all sapphire wafers were heated under $H_2$ flow for 5 minutes at 1110 °C for thermal cleaning of the surface. Then nitridation of the surface was performed under 67 mmol/minute ammonia flow for 7 minutes at the same temperature of 1110 °C. GaN deposition took place as the subsequent step (Table 1). To verify the polarity of our layers, the samples were wet chemically etched in an aqueous KOH solution (5 mol/liter) at 80 °C for 50 minutes [4]. Low temperature photoluminescence (LT-PL) with a laser spot size of 150 µm was used for determination of the layer quality in addition to high resolution X-ray diffraction (only for totally coalesced layers).

**Table 1:** Growth parameters for GaN grown directly on nitridated sapphire. Growth temperature and V/III ratio have been varied within the investigations.

| Growth parameter | |
|---|---|
| Time (min.) | 10 |
| Pressure (hPa) | 100 |
| Temperature (°C) | 920–1110 |
| V/III | 45–1000 |
| Carrier gas | $N_2/H_2$ (1:2) |

## 3. Effect of Nitridation

Our first question was to check the effect of nitridation on the polarity and quality of our layers. The growth procedure described in the experimental section using a GaN growth temperature of 1000 °C and V/III ratio of 120 was applied twice, namely, with and without a nitridation step prior to GaN growth. The layer grown without nitridation (Fig. 1 (b)) had a reduced degree of coalescence compared to its counterpart grown on a nitridated sapphire (Fig. 1 (a)). But most importantly, reconsidering the afore-mentioned comparison, very little of the grown GaN was etched after the KOH test for the layer without nitridation (Figs. 1 (c) and (d)). This indicated a clear influence of the nitridation step on the etching rate in the aqueous KOH solution and hence the chemical reactivity of the surface (as a verification sign for N-polarity of the layer). In addition, skipping the nitridation step resulted in lower crystal quality due to the very strong broad yellow luminescence and the broad GaN band-edge luminescence with 142 meV linewidth (Fig. 2). Grandjean et al. [5] observed a strong variation of the surface lattice parameter of the sapphire to confirm the existence of the AlN layer using reflection high-energy electron diffraction. This surface layer also was confirmed to facilitate the nucleation of GaN

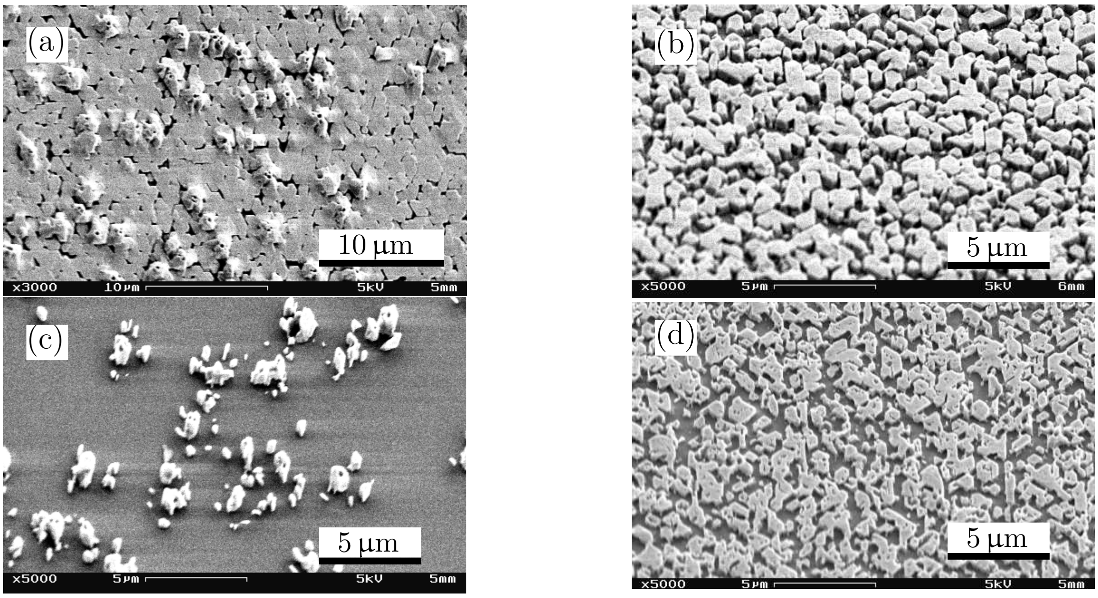



**Fig. 1:** Scanning Electron microscope (SEM) pictures of GaN grown for 10 minutes directly on sapphire at 1000 °C with and without a nitridation step prior to GaN growth, before (a,b) and after (c,d) etching in aqueous KOH solution (5 mol/liter) at 80 °C for 50 minutes, respectively.

on such a nitridated surface rather than on bare sapphire, thus enhancing its respective crystal quality and dictating the polarity orientation of the overgrown crystal. Future work is planned to check the influence of duration, temperature and ammonia supply during the nitridation process on the orientation and crystal quality of the GaN layers.

## 4. Effect of Temperature

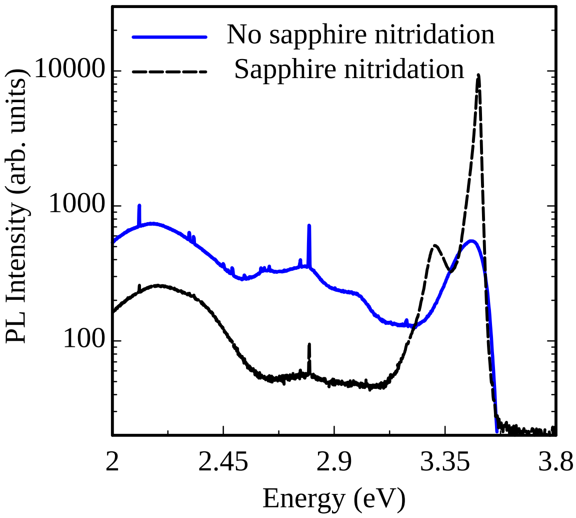



**Fig. 2:** LT-PL spectrum of GaN grown for 10 minutes directly on sapphire with and without a nitridation step at 1000 °C.

A set of three samples grown at the temperatures of 1110 °C, 1000 °C and 920 °C were grown using the parameters shown in Table 1 with a V/III ratio fixed at 120. As shown in

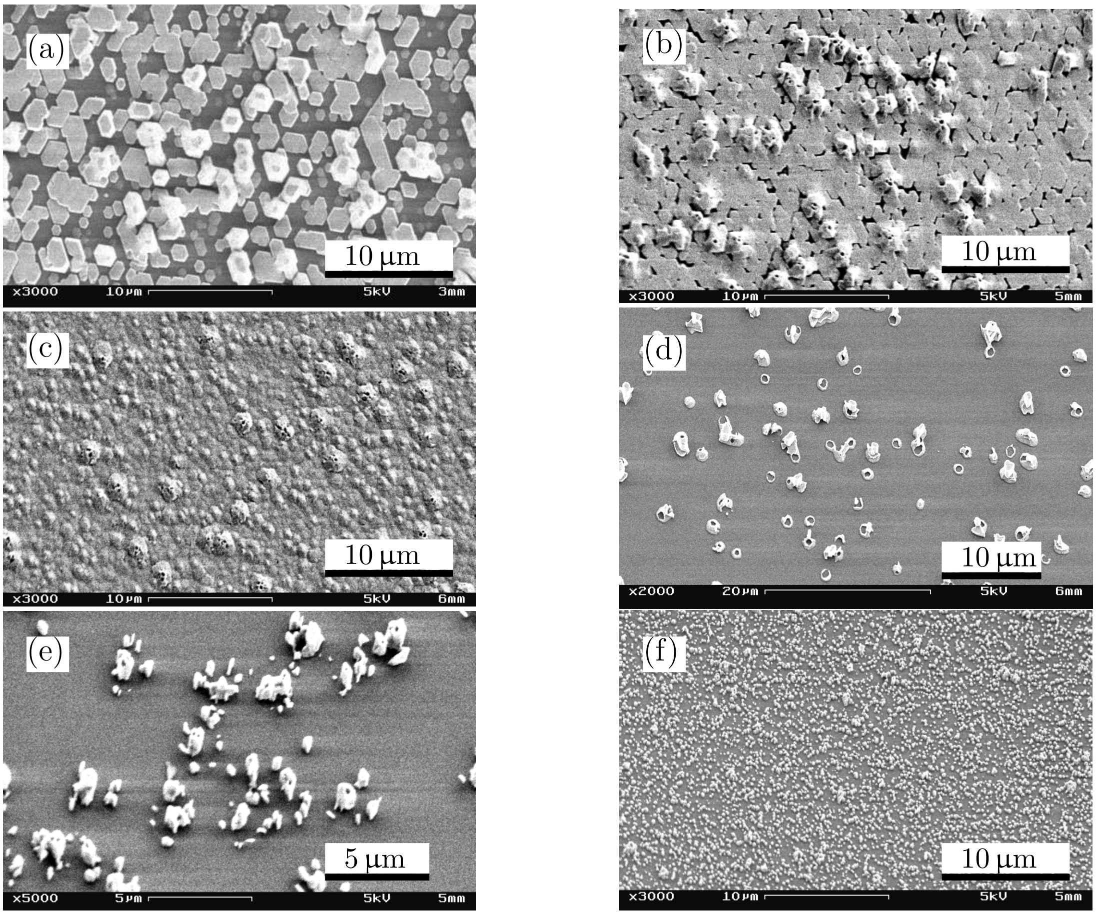



**Fig. 3:** SEM pictures of GaN grown for 10 minutes directly on nitridated sapphire at 1110 °C (a), 1000 °C (b) and 920 °C (c) before and after etching in aqueous KOH solution (5 mol/liter) at 80 °C for 50 minutes (d), (e) and (f), respectively.

Fig. 3 (a), the growth at 1100 °C was characterized by a large number of separated GaN micro-hexagonal structures. Also, the coalescence of the layer showed an inverse relation with temperature (Figs. 3 (a), (b) and (c)). The degree of N-polarity of the grown GaN, however, showed more N-polar nature at higher temperatures due to the observed higher etching rate of the structures (Fig. 3 (d)). In LT-PL (Fig. 4), we were able to observe the narrowest band-edge emission of GaN with 25 meV for the sample grown at 1000 °C. A second weak-intensity peak at 3.33 eV was observed for the afore-mentioned samples that is assumed to be related to prismatic stacking fault luminescence [8]. The sample grown at 920 °C showed the weakest band-edge and the strongest yellow luminescence intensities, respectively, indicating a poorer material quality. The yellow luminescence is believed to originate from either atomic crystal vacancies or carbon impurities (as reported in [9], pp. 19–34 and the references therein). This is expected to be due to the lower degree of atomic surface mobility of atoms to find their energetically favored sites in the crystal as well as the reduced precursor cracking efficiency at lower temperatures. We also believe that at temperatures above 1100 °C, a higher rate of atomic desorption from the surface results hindering the layer coalescence. This is in addition to the fact that sapphire nitridation as the formation of a relaxed AlN layer [5] (as described in

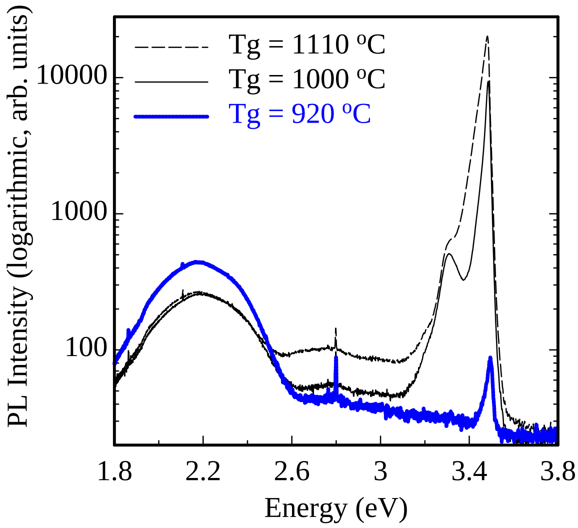
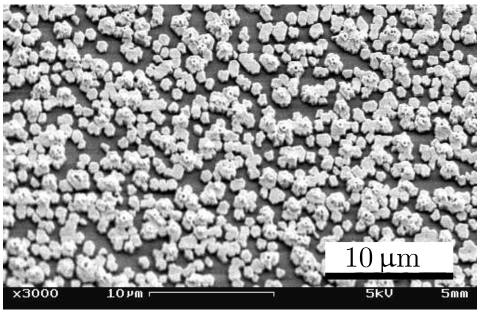



**Fig. 4:** LT-PL spectra of GaN grown for 10 minutes directly on nitridated sapphire at growth temperatures (Tg) of 1110, 1000 and 920 °C.



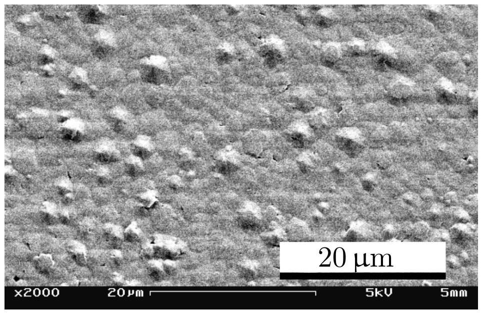




**Fig. 5:** SEM pictures of GaN grown for 10 minutes directly on nitridated sapphire at 1000 °C with V/III ratios of 1100 (left) and 45 (right).

the previous section) is believed to be constantly effected even during growth at this high temperature regime. Hence, it dictates the N-polar nature of the firstly grown GaN monolayer islands and consequently, the overgrown crystal. As a conclusion, this series confirmed that within the growth temperature range of 900–1150 °C typical for GaN layers, direct growth at higher temperatures result in lower coalescence and growth of vertical micro-hexagonal structures with a large degree of N-polarity, while GaN growth at lower temperatures result in coalesced layers but lower degree of N-polarity and lower crystal quality.

## 5. Effect of V/III Ratio

We further proceeded with reproducing again our best sample in the temperature series (grown at 1000 °C) showing narrowest linewidth and highest layer coalescence, however, using the V/III ratios of 1100 and 45. As shown in Fig. 5, the lower V/III ratio enhances layer coalescence to a very large extent, while the opposite behavior is observed for higher V/III ratios. The thickness of the coalesced layer grown using the V/III ratio of 45 was measured using optical interference reflectance to be 170 nm. In high resolution X-ray diffraction, the values of 1600 arcseconds and 1550 arcseconds were measured for

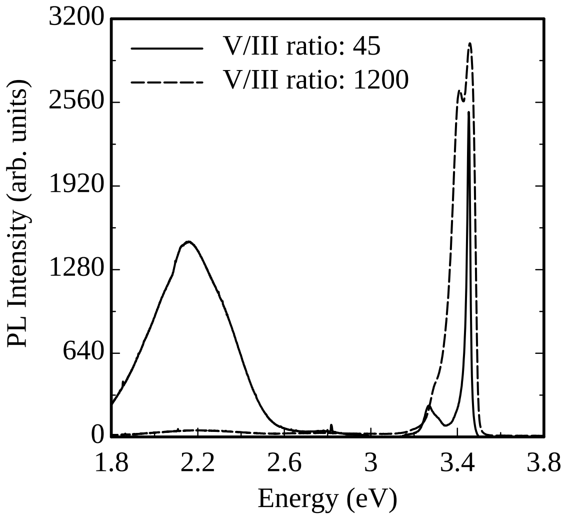



**Fig. 6:** LT-PL spectra of GaN grown for 10 minutes directly on nitridated sapphire at 1000 °C with V/III ratios of 1100 and 45.

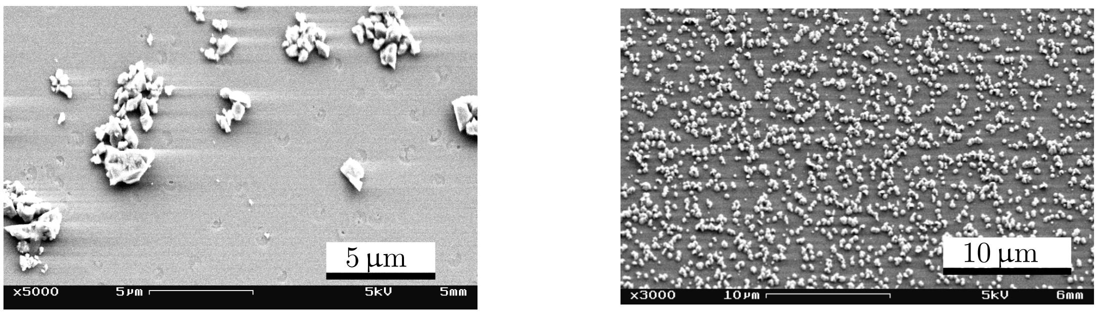



**Fig. 7:** SEM pictures of GaN grown for 10 minutes directly on nitridated sapphire at 1000 °C under V/III ratios of 45 (left) and 1100 (right) after etching in aqueous KOH solution.

the symmetric (0002) and asymmetric (102) reflections, respectively. It is expected that the latter values will improve to large extents if the layer thicknesses are above[2] 2 µm. Moreover, a narrower linewidth of 20 meV is measured for the totally coalesced layer with V/III ratio of 45 (Fig. 6). However, the latter sample showed stronger yellow luminescence which is assumed to result from atomic vacancies due to reduced supply of ammonia. In addition, the GaN grown at higher V/III ratio showed a strong emission around 3.41 eV indicating the presence of basal plane stacking faults[3] [8]. After the KOH test, more etching of the grown GaN is observed for the sample grown under higher V/III ratio (Fig. 7). Therefore, we conclude that high N precursor supply during nucleation is necessary for the realization of N-polar crystal orientation in the layer. This investigation showed that direct GaN growth under very low V/III ratios enhances lateral growth and layer coalescence, but results in a lower degree of N-polarity.

[2]A thicker layer around 750 nm grown using same conditions (not shown here) revealed the values of 920 arcseconds and 840 arcseconds for the symmetric (0002) and asymmetric (102) reflections, respectively, however with very high surface roughness. Investigations are ongoing for further optimization of surface roughness and crystal quality.

[3]However, in c-plane growth basal plane stacking faults are typically not critical, as they are aligned in the c-plane and hence get buried at larger layer thickness.

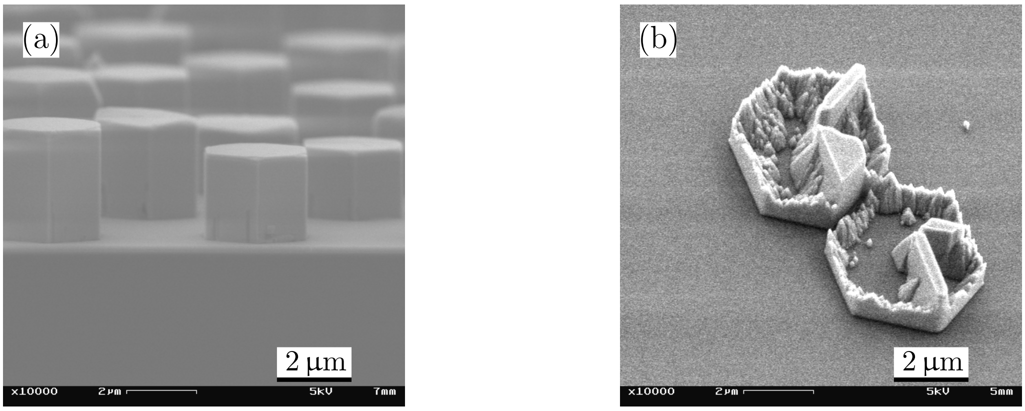



**Fig. 8:** Selectively grown GaN micro-rods on patterned sapphire using an $SiO_2$ mask before (a) and after (b) etching in aqueous KOH solution.

## 6. Selective Area Epitaxy of N-polar GaN

As reported in [4], selectively grown N-polar GaN structures on masked substrates typically favor vertical growth with non-polar planes developing as side facets. This is in comparison to pyramidal structures with semi-polar side facets typically observed for Ga-polar selectively grown GaN. Thus, we wanted to test our growth conditions for GaN layers on a masked sapphire substrate for realizing the afore-mentioned N-polar vertically grown hexagons. We have chosen the same parameters described in Table 1 with a temperature of 1110 °C and a V/III ratio 160 on sapphire substrate masked with 100 nm $SiO_2$ with circular openings of 3 μm diameter[4]. As shown in Fig. 8 (a), the expected vertical growth was achieved. The KOH test showed that most of the vertically grown micro-structures were etched (Fig. 8 (b)). However, GaN with lower etch rates was still observed within the micro-rods, indicating the existence of inversion domain boundaries. The vertical growth of the selectively grown GaN rods further confirmed that the growth procedure described in Table 1 leads to GaN growth with predominantly N-polar crystal orientation.

## 7. Conclusion

We have investigated the influence of temperature, nitridation and V/III ratio on the polarity, quality and coalescence of thin nucleation GaN layers (around 170 nm) on c-plane sapphire by metal organic vapor phase epitaxy (MOVPE). It was shown that higher temperatures (above 1100 °C) result in lower coalescence and growth of vertical micro-hexagonal structures with a large degree of N-polarity, while lower temperatures (below 950 °C) resulted in coalesced layer but lower degree of N-polarity and lower crystal quality. Moreover, initial nitridation of the sapphire before GaN growth proved to be critical for achieving N-polar growth and improving the crystal quality. A lower V/III ratio (below 50) at a temperature of 1000 °C showed complete layer coalescence and a linewidth of

[4]The high temperature was chosen to enhance the degree of N-polarity of the selectively grown GaN structures.

20 meV for the GaN band-edge emission, whereas a higher V/III ratio of 1100 resulted in GaN structures separated from one another. Finally, vertical GaN micro-rods selectively grown on patterned sapphire were mostly etched in aqueous KOH solution proving the dominant N-polar exhibiting mainly N-polar growth.

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