# Polarity Control of GaN Films Grown by Metal Organic Chemical Vapor Deposition on (0001) Sapphire Substrates

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## ABSTRACT

The polarity control of GaN films grown on c-plane sapphire substrates by low pressure metal organic chemical vapor deposition (MOCVD) was achieved by using $N_2$ as a diluent and transport gas. The type of polarity was governed by the substrate treatment prior to the GaN growth. N-face (-c) GaN films were only obtained by pre-nitridation of the sapphire substrate after a $H_2$ anneal, while Ga-face (+c) GaN films were grown directly on the substrates or on properly annealed AlN buffer layers. In addition, GaN films on improperly annealed AlN buffer layers, that is, under- or over-annealed buffer layers, yielded films with mixed polarity. Smooth N-face GaN films with 2.5 nm RMS roughness, as determined by atomic force microscopy (AFM), were obtained with shorter nitridation times (less than 2 min). Wet chemical etching in an aqueous solution of potassium hydroxide (KOH) was used to determine the polarity type.

## INTRODUCTION

III-nitride semiconductors crystallizing in a wurtzite crystal structure possess a polar axis oriented along the <0001> direction. This polarity is a consequence of the non-centrosymmetric crystal structure of the III-nitrides. The most common growth direction of the III-nitrides is normal to the {0001} basal plane, where the atoms are arranged in bilayers consisting of two closely spaced hexagonal layers, one containing the cations and the other anions, so that the bilayers have polar faces, as shown in Figure 1.

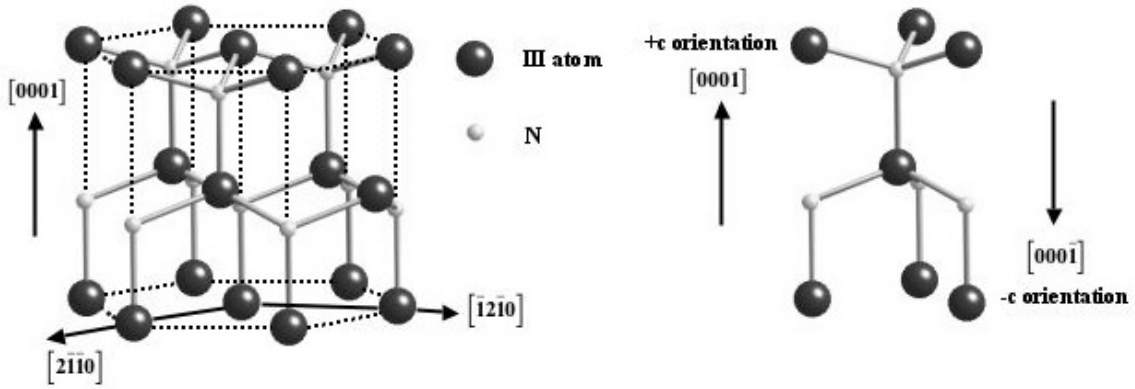


**Figure 1.** Crystal structure and partial unit cell of a wurtzite III-nitride semiconductor.

The polar faces in GaN are commonly referred to as the Ga- (+c orientation) or N-face (-c orientation). Ga-face indicates the polar structure with three bonds of the nitrogen that point up, while N-face indicates single bond that points upward. Polar orientation should not be confused with surface termination, as each orientation may be terminated with either one of the species. In short, the two polarities are related by an inversion operation, which is a true symmetry operation. The surface atomic configuration and neighboring atom arrangement are different between the Ga-face and N-face. This difference in surface structure has an influence on the growth mode of wurtzite GaN, as well as on the development of potential GaN materials for device applications. Therefore, it is very important to be able to determine and control the polarity of GaN films.

Polarity control of MOCVD GaN films can be managed by systematic substrate treatments consisting of nitridation, buffer layer deposition, and buffer layer anneal time [1]. Each step has an influence on the subsequent process. N-face films are obtained when GaN films are grown on nitrided substrates, even after nitridation lasting only a few seconds. As for Ga-face, the low temperature (LT)-buffer layer plays a great role in controlling the polar orientation of the GaN films. Ga-face GaN can be obtained by optimizing the thickness of the buffer layer and by using the proper anneal conditions. GaN films on improperly treated LT-buffer layer lead to N-face or mixed face polarity. The polarity of GaN films can be inferred from the surface morphology: the surface of Ga-face GaN is either very flat or shows stepped terraces, often with pits, while that of N-face GaN contains hexagonal facets. The easiest method of determining the polarity type is wet chemical etching using alkali solutions such as KOH and NaOH [2]. N-face GaN is etched in alkali solutions, while Ga-face GaN is inert to etching in these solutions.

N-face GaN films, in general, present a rough surface morphology featuring hexagonal facets and grow slower than Ga-face GaN films [3]. The reason responsible for this may be the use of $H_2$ as a dilution gas, which is commonly used in the MOCVD processes. Above 900°C, standard GaN growth temperatures, the growth rate is temperature independent if a $N_2$ ambient is used; in contrast, it is reduced by approximately 50% between 900 and 1100°C under a $H_2$ ambient [4]. This suggests that under a $N_2$ atmosphere, the growth is mass-transfer limited, while under $H_2$ it is reaction-rate limited. In terms of CVD growth, high quality films are desirable to be grown at the growth temperatures dominated by the mass-transfer limited region. Thus, the use of $N_2$ as a diluent and transport gas would lead to smooth N-face GaN films and the same growth rate for both faces.

In this paper, a scheme for controlling the polarity type of GaN films in MOCVD growth will be presented. In addition, the role of nitrogen as a transport and dilution gas for the growth of Ga-face and smooth N-face GaN films with equal growth rates will be discussed.

## EXPERIMENT

All the films for these experiments were grown in a vertical, cold-wall, RF-heated, low-pressure MOCVD reactor. The reactor base pressure was $1\times10^{-7}$ Torr. Triethylgallium (TEG), Trimethylaluminum (TMA) and Ammonia were used as Ga, Al, and N precursors, respectively. $N_2$ was used as a diluent and transport gas throughout the growth process. Two inch-diameter, (0001)-oriented sapphire wafers were used as substrates. After the wafer was annealed in vacuum, it was $H_2$ annealed at 1090°C. Growth conditions for controlling the polarity type of GaN films are summarized in Table I. Our standard conditions consisted of a TEG flow of 36 μmol/min, an Ammonia flow of 0.4 slm and a total flow of 2.15 slm at 20 Torr of total pressure.

**Table I.** Growth conditions for the control of the polarity type in GaN films: (a) Ga-face GaN and (b) N-face GaN.

(a) Ga-face GaN growth conditions.

| $H_2$ cleaning 1090°C | Nitridation 930°C | LT-AlN buffer 600°C | Buffer anneal 600~1030°C | HT-GaN 1030°C |
|---|---|---|---|---|
| 10 min Surface treatment | 2 min | 5 to 10 min V/III ratio: 24500 Thickness: 20 to 40nm | 20 min $NH_3$ : $N_2$ = 0.4:1.6 slm | 30 min V/III ratio:500 $NH_3$ : $N_2$ = 0.4:1.6 slm Thickness: 0.6 μm |

(b) N-face GaN growth conditions.

| $H_2$ Cleaning 1090°C | Nitridation 930°C | HT-GaN 1030°C |
|---|---|---|
| 10 min | 30sec~5 min | Same as Ga-face GaN |

High-temperature (HT) GaN growth was carried out at 1030°C. These conditions provided a V/III ratio of 500 and a growth rate of 1.2 μm/h. A nitridation step prior to LT AlN buffer layer deposition was necessary to control the polarity. The AlN buffer layer, grown at 600°C, was 20 to 40 nm thick. No buffer layer was used to grow N-face GaN films, while a proper buffer layer anneal after deposition was necessary to obtain Ga-face GaN films. The anneal time refers to the time interval from the end of the buffer layer grown at 600°C until the start of the HT GaN growth at 1030°C. The polarity of all samples was determined by wet etching in a KOH solution. The sample was placed in a 3M KOH solution at 65°C and afterwards observed in an optical microscope. Atomic force microscopy (AFM) images were acquired using a JEOL JSPM-5200 in the AC mode (i.e., tapping). Crystallographic characterization was performed by acquiring on- and off-axis HRXRD rocking curves using a Philips X'Pert Materials Research Diffractometer with a copper x-ray source operated at 40 kV and 45 mA and an open slit on the detector side.

## RESULTS AND DISCUSSION

Under the conditions described in the previous section, growth rates for both polarity faces were found to be identical regardless of the substrate treatment prior to HT GaN growth. A V/III ratio as low as 500 was used, while the growth rate was maintained at 1.2 μm/h for all GaN films. This result is different from general observations that Ga-face grows faster than the N-face [3]. Mirror-like, Ga-face GaN films were obtained at a V/III ratio of 500 with 20 min annealed LT AlN buffer layers. The full width at half maximum (FWHM) of Ga-face GaN films was 371 arcsec for the (10.5) skew-symmetric reflection and 548 arcsec for the (00.4) symmetric reflection; the surface roughness was measured by AFM as 0.2 nm RMS. These results demonstrate that by using $N_2$ as the only diluent gas, one can achieve films of the same quality as by using $H_2$ dilution.

**Table II.** Survey of etching results.

| Sample | Nitridation | LT-AlN buffer | Buffer anneal | KOH solution | Polarity type |
|---|---|---|---|---|---|
| A | 30s | × | × | etch | N-face |
| B | 1 min | | | | |
| C | 2 min | | | | |
| D | 5 min | | | | |
| E | × | × | × | lift-off | Ga-face |
| F | 2min | 40nm | 20min | inert | Ga-face |
| G | | 20nm | 20min | etch | mixed-face |

Growth results of films of different polarity are summarized in Table II. The polarity was determined by wet chemical etching using 3M KOH solutions. GaN films grown directly on sapphire substrates exhibited the Ga-face (e.g. sample type E). Lift-off indicates that there was delamination of the epitaxial film rather than etching. It is assumed that the etch solution attacked the interface, which accumulated a high density of stacking faults and dislocations due to lattice mismatch. This reaction occurred preferably at defect locations [5]. On the other hand, films grown on nitrided substrates showed a N-face. The nitridation step resulted in (-c)-oriented GaN films. Nitridation times were as short as 30 sec. This step formed an AlN monolayer, which promoted -c polarity by theoretical calculations [6]. The following HT-GaN films on nitrided substrates showed the N-face polarity. As for GaN films grown on LT-AlN buffer layers, the polarity type of GaN films strongly depended on the buffer anneal time. Properly annealed buffer layers resulted in Ga-face films with a mirror-like surface morphology. This treatment yielded an optimized 40 nm thick LT-AlN buffer layer in a time of 20 min. Sample type G, GaN film on 20 nm thick and 20 min annealed buffer layer, showed mixed-face polarity. In addition, if further annealing was conducted, GaN films led to completely N-face GaN films due to a complete evaporation of the LT-AlN buffer layer during the anneal step. 40 nm-thick, under-annealed buffer layers (shorter than 20 min anneal), also resulted in the growth of mixed-face GaN films (not showed in Table I). Mixed-face films contained small domains of both polarities. At the same time, mixed-face films showed slower etching rates compared to the N-face films. Mixed-face GaN films were likely to be obtained by improper buffer anneal time. Our results of polarity management of GaN films by using $N_2$ as a diluent and transport gas are similar to the results obtained by using $H_2$ dilution [1].

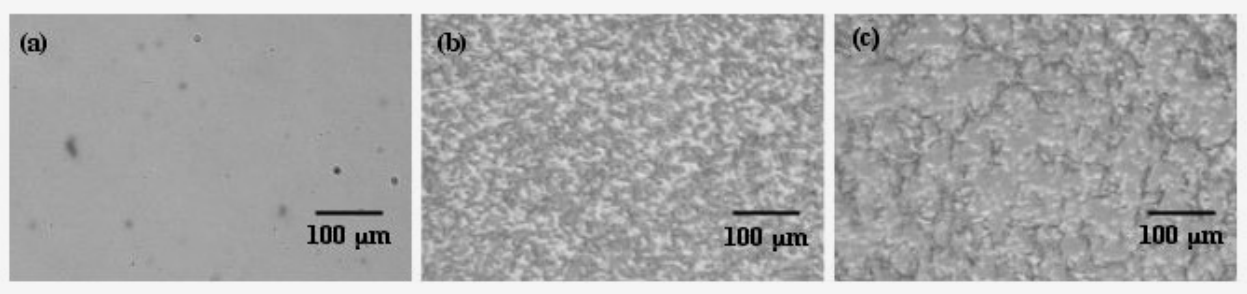


**Figure 2.** Optical micrographs of N-face GaN before and after KOH etching: (a) as-grown, (b) after etching for 10 min, and (c) after etching for 20 min.

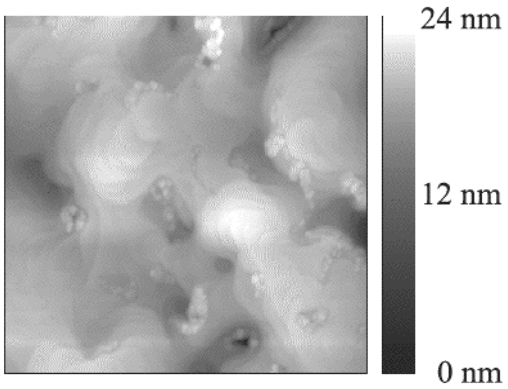


**Figure 3.** AFM image of a 0.6 μm thick N-face GaN film grown on 1 min-nitrided substrate.

Figure 2 shows optical micrographs of a 0.6 μm thick GaN film grown on a nitrided (30 s) sapphire substrate at a V/III ratio of 500, before and after dipping into a 3M KOH solution. Although there were often pits on the as-grown surface, no hexagonal facets were found on the film. The surface morphology was drastically changed with the increase of etching time, which indicated N-face polarity. In contrast, the surface morphology change of Ga-face GaN films was hardly detected even after 2 hr of etching in the same solution (not shown here). The AFM images of N-face GaN films exhibited the step-flow growth mode with a step-height of 0.4 nm and randomly distributed pits and bumps, as shown in Figure 3. The bump density of the film was on the order of $10^9$ $cm^{-2}$, which is comparable to that reported for threading dislocation densities in GaN films. The surface roughness was calculated to be 2.5 nm RMS for N-face GaN films. It is a prevalent belief that the use of $N_2$ as the only diluent produces rough GaN films with a mosaic structure [4]. In contrast, our results demonstrate that using $N_2$ as the only diluent and optimized V/III ratio as low as 500 enable growth of smooth N- and Ga-face GaN films.

Atomic species involved in the growth of GaN films consist of Ga, $NH_3$ $H_2$, RH ($CH_4$ or $C_2H_6$) and $N_2$. The growing surface at the gas-solid interface is expressed by equation (1).

$$Ga\,(g) + NH_3\,(g) \rightarrow GaN\,(s) + 3/2\,H_2\,(g) \qquad (1)$$

Ga species directly react with $NH_3$, as shown in equation above. $H_2$ is produced along with the formation of GaN. The growth of GaN films seems to be influenced by the hydrogen partial pressure in the reactor. The use of $H_2$ as a transport gas increases the partial pressure of hydrogen, and as a result, enhanced etching of GaN occurs via reaction with the atomic and molecular hydrogen derived from the dissociation of the ammonia and $H_2$ diluent [7]. This is one of the reasons that high V/III ratios (e.g. >2000) should be necessary for III-nitride materials. Dilution with $N_2$ reduces the partial pressure of hydrogen, thus, a V/III ratio of as low as 500 enables not only Ga-face GaN films but also N-face GaN to have smooth surfaces. It is expected that process optimization will further improve film quality, especially in terms of a lower V/III ratio.

## CONCLUSIONS

GaN films were grown on sapphire substrates from TEG and $NH_3$ precursors by using a V/III ratio of less than 500, and $N_2$ as a transport and dilution gas. Smooth films of both types of polarity with the same growth rate were obtained by optimizing the initial treatment of the sapphire substrates, i.e., the substrate nitridation and the LT-AlN buffer layer anneal time.

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