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Nucleation and epitaxial growth of ZnO on GaN(0001)

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ABSTRACT

Plasma-assisted molecular beam epitaxy was used to grow ZnO(0001) layers on GaN(0001)/Al_2O_3 templates and GaN/4H-SiC(0001) layers. The GaN(0001)/Al_2O_3 template surfaces were subjected to various pre-treatment procedures (Zn, Ga or N pre-exposure or none) prior to the ZnO growth. We studied the impact of these pre-treatment procedures on the initial growth conditions of ZnO(0001). These layers were compared to ZnO layers deposited on 4H-SiC utilizing a GaN(0001) buffer layer that was grown in situ on the 4H-SiC substrate and immediately before the growth of ZnO. The GaN buffer layers were not pre-treated or exposed to ambient. Atomic force and scanning electron microscopy as well as secondary ion mass spectroscopy revealed that the pre-treatment procedures resulted in a very high density of islands. The islands coalesced into films as the growth progressed. In contrast, no ZnO growth occurred on the untreated GaN(0001)/Al_2O_3 template surfaces. Our main finding is that Ga_xO_y sub-oxides residing on the surface of the as-received GaN-templates, drastically reduced the ZnO nucleation rate and completely inhibited subsequent coalescence and growth. Our various surface pre-treatment procedures aimed at removing the sub-oxides were necessary for achieving ZnO growth on the GaN-templates. No surface pre-treatment was needed to enable ZnO growth on the in situ grown GaN(0001)/4H-SiC layers.

1. Introduction

The many similarities between the two wide-bandgap semiconductors GaN and ZnO should in principle, offer many advantages by combining them. For instance, the lattice mismatch is only 1.9% which is small for this system. In addition, both GaN and ZnO have the same wurtzite crystal structure meaning that phase separation does not arise. Many research groups have indeed reported on the growth of ZnO on GaN with various techniques such as pulsed laser deposition (PLD) [1], molecular beam epitaxy (MBE) [2] and metalorganic chemical vapor deposition (MOCVD) [3].

Early reports describe the impact of pre-exposing the GaN/Al_2O_3 template layers to Zn or O (prior to the ZnO growth) on the structural quality, interface homogeneity and resulting polarity (Zn- or O-face) [4–9]. The conclusion in these early reports is that Zn pre-exposure yielded better results in terms of structural quality and interface homogeneity. The Zn pre-exposure also always resulted in Zn-face ZnO. The O pre-exposed samples on the other hand resulted in the formation of monoclinic Ga_2O_3 at the interface that in turn yielded a lesser structural quality and O-face ZnO.

Little attention has been focused on how the condition of the GaN surface affects the initial ZnO nucleation and growth. A proper nucleation is crucial in achieving high-quality ZnO epitaxial layers since the initial stages of the growth have a profound impact on the progress of the subsequent growth process. It is therefore important to study how the initial growth proceeds depending on the condition of the GaN surface, which can be altered through various pre-treatments.

In this paper, we investigate the impact of different surface pre-treatment procedures of the GaN surface on the following ZnO nucleation and growth. We found, by comparing ZnO layers grown on GaN/Al_2O_3 templates with ZnO deposited on in situ grown GaN/4H-SiC layers, that surface Ga_xO_y sub-oxides play a crucial role for the rate of the ZnO nucleation and film coalescence. It also strongly affects the surface morphology. Our GaN/4H-SiC layers were never exposed to the ambient and therefore never formed sub-oxides. The pre-treatment procedures aimed at removing these sub-oxides on the GaN(0001)/Al_2O_3 templates were vital to achieve growth of ZnO.

2. Experiment

All ZnO-layers were grown with a plasma assisted MBE system equipped with an O-plasma source (Veeco) supplied with 6N O_2 for producing active O. Elemental Zn was provided by

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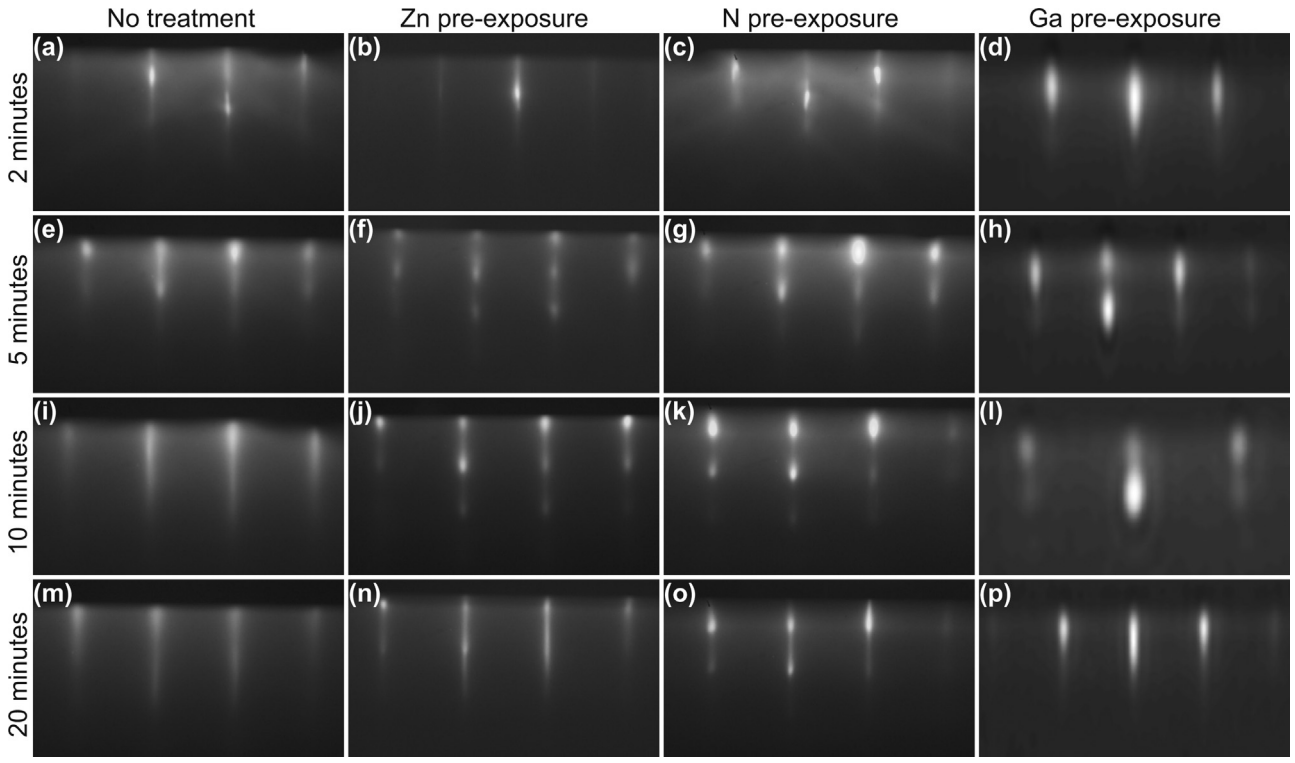

Fig. 1. Temporal evolution of RHEED patterns of the ZnO growth on GaN/Al_2O_3 templates from [11$\bar{2}$0] azimuth. Each column corresponds to a certain pre-treatment procedure which also is indicated. The rows each correspond to 2, 5, 10 or 20 min growth, respectively. The surface of each GaN/Al_2O_3 template was air-exposed before each pre-treatment.

a solid source effusion cell filled with 6N Zn. The MBE base pressure was 2×10^{-9} mbar while the pressure during growth was 1.4×10^{-5} mbar. The Zn beam equivalent pressure (BEP) was 1×10^{-5} mbar and the O_2-flow was regulated to 2 standard cubic centimeters per minute (sccm) for a plasma power of 300 W. A reflection high-energy electron diffraction (RHEED) apparatus attached to the MBE growth chamber was used to monitor the effect of the pre-treatment procedures on the GaN surface and the following ZnO growth. The growth of the GaN/4H-SiC(0001) buffer layers was performed in the same MBE chamber which is equipped with a N-plasma source (Veeco) supplied with 7N N_2 for producing active N. The N-plasma source was operated at 250 W with a N_2-flow of 0.5 sccm. A solid source effusion cell loaded with 7N Ga was used to provide elemental Ga. The Ga-BEP was 2×10^{-6} mbar. Sample rotation was enabled for all growths.

The GaN(0001)/Al_2O_3 templates (St. Gobain Crystals) with a nominal GaN thickness of 3.5 μm were cleaved into 15×15 mm^2 pieces and degreased using a standard organic cleaning procedure (acetone, isopropanol, de-ionized H_2O, sonication, N_2 blow-dry) before mounting with In onto Si wafers that in turn were attached to the Mo holders used in the MBE system. The Si wafers were coated with 2 μm Ti on the back side to improve the thermal uniformity. The same mounting procedure was used for the 4H-SiC(0001) substrates (acquired from CREE and polished by NOVASiC).

The GaN templates were outgassed at 500–600 °C for 1–3 h in the growth chamber before the growth. All templates exhibited bright and sharp RHEED streaks with Kikuchi lines and an intense specular spot. Before the ZnO nucleation growth was initiated, the GaN templates were subjected to one of the four pre-treatments described in the following:

1. *No treatment*: The substrate temperature was immediately increased to 700°C before starting the ZnO nucleation.
2. *Zn pre-exposure*: Zn was deposited on the GaN template at 280°C. We stopped the deposition when the RHEED-intensity decreased. The substrate temperature was then increased to 870°C. The Zn-shutter was opened and closed in 5 s intervals continuously during the temperature ramp up. The RHEED streaks became sharper and more intense during the ramp. Finally, the substrate temperature was decreased to the growth temperature of 700°C and the ZnO nucleation growth was initiated.
3. *N pre-exposure*: The N-plasma source shutter was opened and closed in intervals of 1–2 s while the substrate temperature was increased to 850°C after which it was immediately decreased to 500°C. At this point the N-plasma shutter was closed, the N-plasma source was turned off and the system was pumped down to 10^{-8} mbar. The substrate temperature was then ramped up to the ZnO nucleation growth temperature of 700°C. The N pre-exposure produced RHEED streaks that were brighter, longer and thinner compared to the RHEED pattern of the as-received and untreated GaN template.
4. *Ga pre-exposure*: Ga was deposited at 600°C until it was almost not possible to observe the RHEED pattern anymore which occurred after 45–60 s. The substrate was then heated to 850°C to desorb the excess Ga. The intensity of the RHEED pattern increased significantly during this procedure. After a few seconds at 850°C the substrate temperature was decreased to the ZnO nucleation growth temperature (700°C).

All ZnO growths on the GaN/Al_2O_3 templates were performed at 700°C and were initiated by first depositing Zn for 1 min on the GaN surface. The O-plasma source was then turned on and the nucleation growth started by opening the O-plasma source shutter. The growths were terminated by closing the Zn shutter and decreasing the substrate temperature to 400°C where the O-plasma shutter was closed and the O-plasma source was turned off. Two main series of samples were produced each corresponding

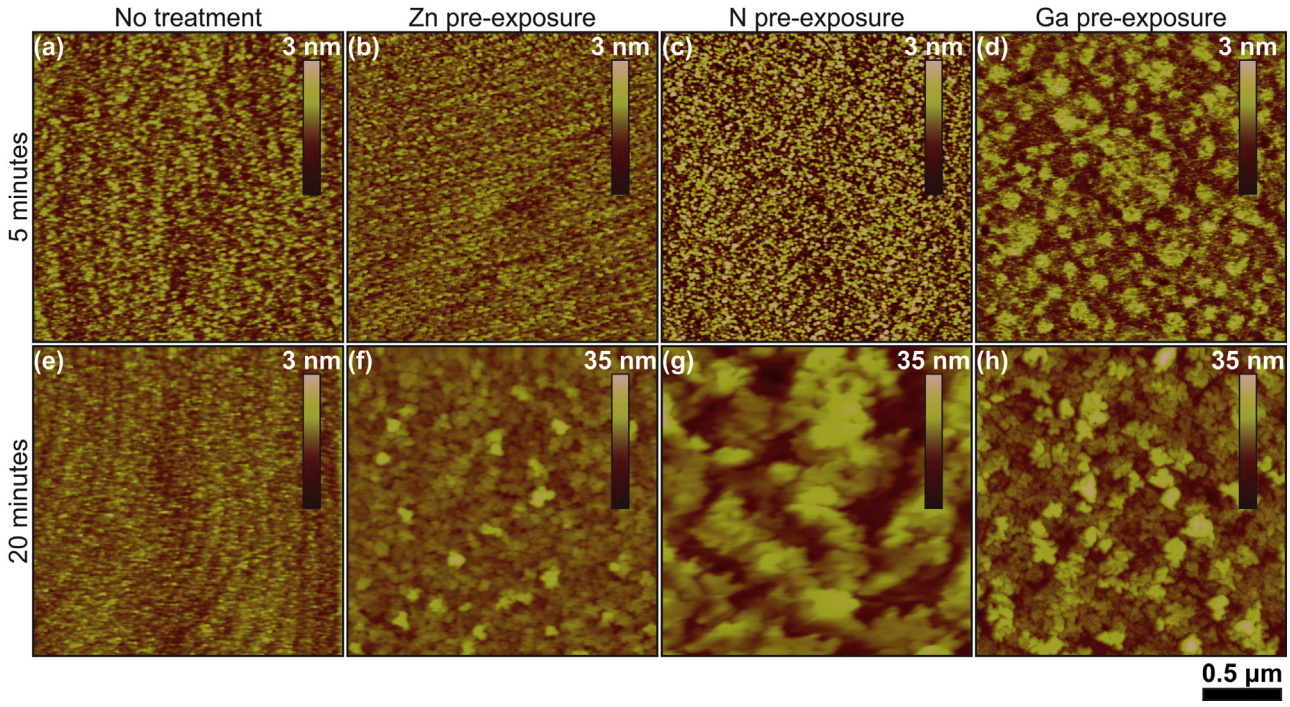

Fig. 2. AFM micrographs of nucleation sample surfaces after 5 (a)–(d) and 20 min (e)–(h) of ZnO nucleation growth on untreated as well as on Zn, N and Ga pre-exposed GaN/Al_2O_3 templates. The surface of each GaN/Al_2O_3 template was air-exposed before each pre-treatment.

to a ZnO deposition time of 5 or 20 min. In addition, a few samples were grown for 2 or 60 min.

The nucleation growths on 4H-SiC were preceded by a 2 h long outgassing of the 4H-SiC substrate at 600°C in the MBE growth chamber. Then Ga was deposited for 45 s when the RHEED pattern almost vanished. The substrate was ramped up to 900°C to desorb the excess Ga. A 3×1 reconstruction was observed at 825°C. The substrate temperature was decreased from 900°C to

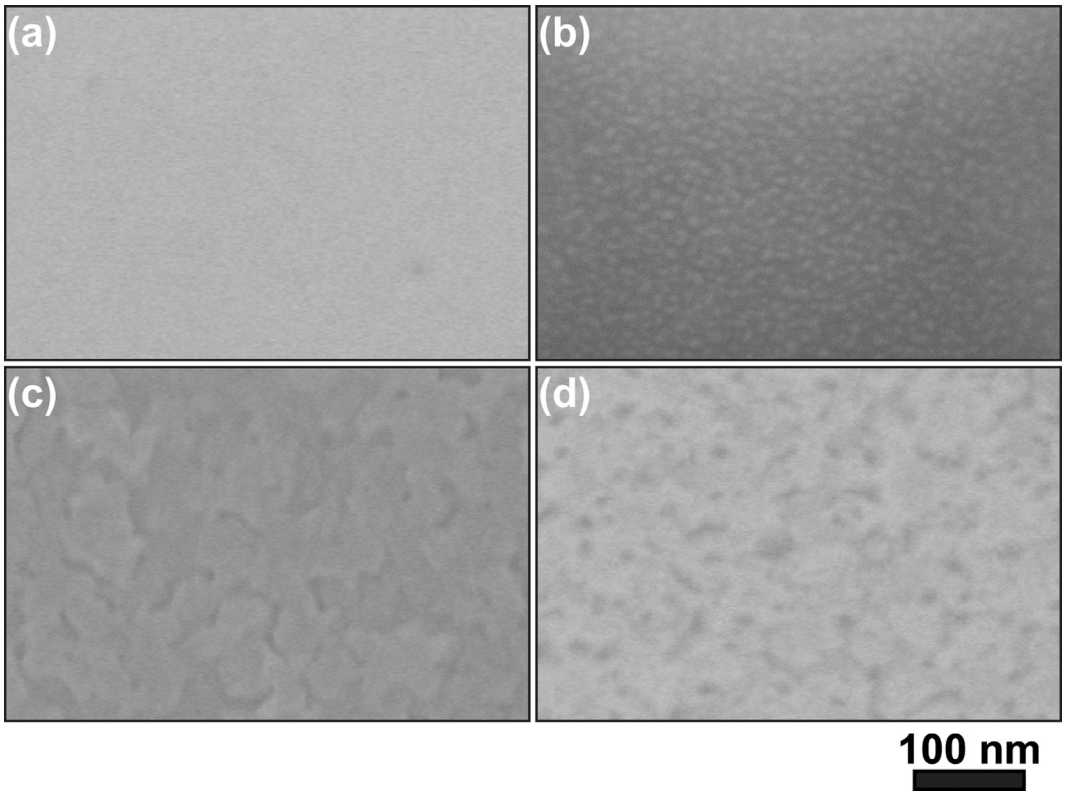

Fig. 3. SEM micrographs of a Ga pre-exposed GaN/Al_2O_3 template surface after 2 (a), 5 (b), 20 (c) and 60 min (d) of ZnO growth. The surface of each GaN/Al_2O_3 template was air-exposed before each pre-treatment.

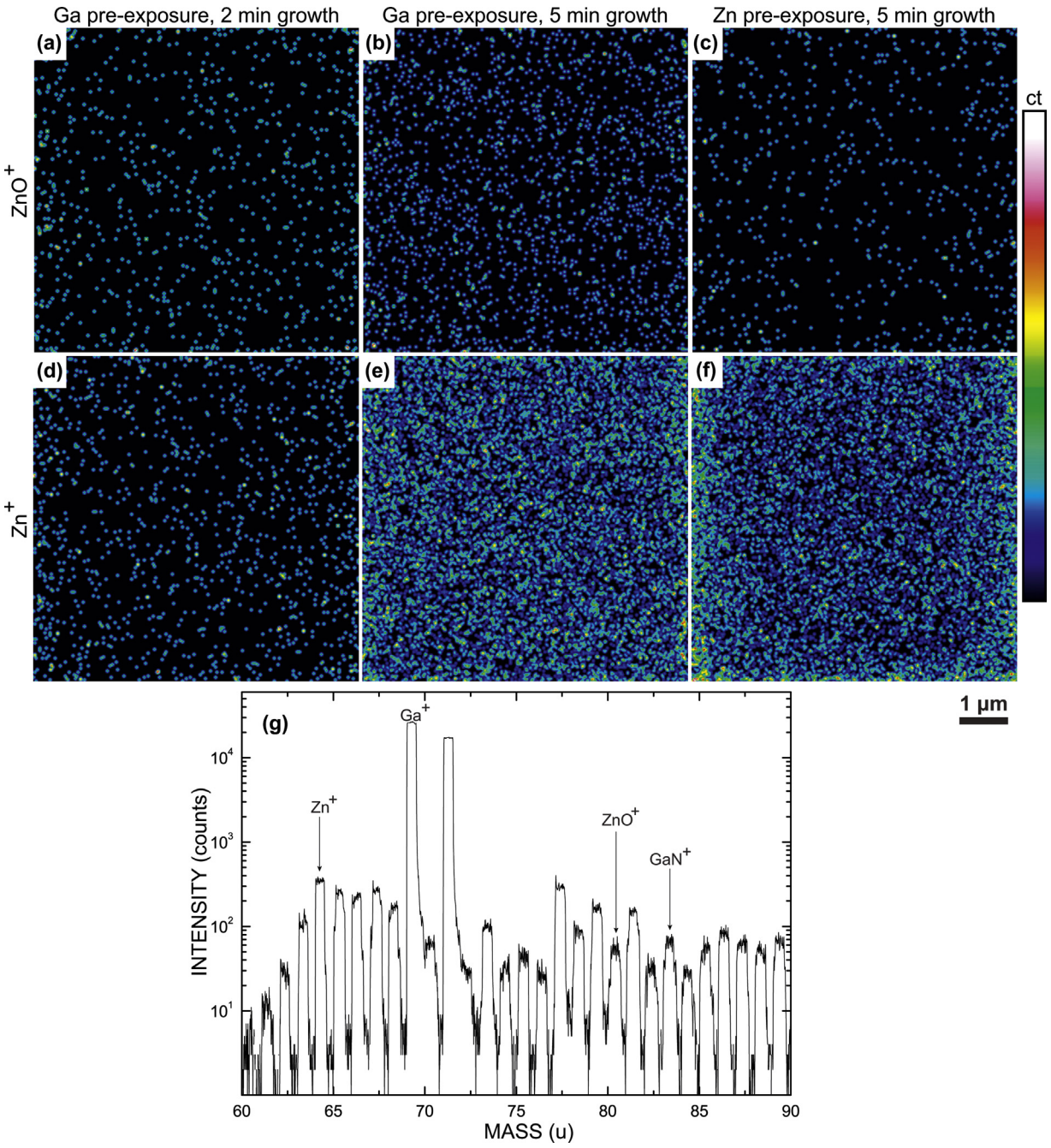

Fig. 4. TOF-SIMS images obtained over areas from the surface of ZnO layers grown for 2 min on Ga pre-exposed GaN/Al_2O_3 templates (a) and (d). The surface after 5 min of growth is shown in (b) and (e). 5 min growth on Zn pre-exposed GaN/Al_2O_3 templates is shown in (c) and (f). The mass spectra for the ZnO layer grown for 5 min on Ga pre-exposed GaN/Al_2O_3 templates (g). The surface of each GaN/Al_2O_3 template was air-exposed before each pre-treatment.

the GaN buffer layer growth temperature of 865°C. The N-plasma source was then turned on and the GaN growth was initiated by opening the Ga- and N-shutters simultaneously. The GaN growth was terminated after 1 h yielding a thickness of 230 nm. The substrate temperature was then decreased to 500°C and the growth chamber pressure was allowed to reach 1.4×10^{-7} mbar before the ZnO nucleation growth started. Long bright sharp RHEED-streaks after the GaN-growth was observed at this stage. The procedure for the ZnO growth was the same as for the growth experiments on the GaN/Al_2O_3 templates with no surface pre-treatment. The ZnO growth was terminated after 1 h yielding a thickness of 135 nm.

The surface morphology was characterized with atomic force microscopy (AFM) and scanning electron microscopy (SEM). Time of flight secondary ion mass spectroscopy (TOF-SIMS) was used to perform elemental analysis of the surfaces while the structural quality was investigated by X-ray diffraction (XRD).

3. Results and discussion

The temporal evolution of the RHEED patterns from the ZnO growths on air-exposed GaN/Al_2O_3 templates is displayed in Fig. 1 for the $[11\bar{2}0]$ azimuth. Each of the four columns in Fig. 1 corresponds to one of the four pre-treatment procedures 1–4 described previously. Each row in Fig. 1 corresponds to either 2, 5, 10 or 20 min of ZnO deposition.

For all growth experiments, immediately after commencing the growth, the Kikuchi lines disappeared and the RHEED streaks

became slightly thicker and diffuse but with the same intensity. The RHEED pattern remained unchanged during the first 2 min [Fig. 1(a)–(d)] for all samples. For the samples grown on substrates subjected to the Zn-, N-, or Ga pre-exposure, the RHEED pattern changed drastically after 4–5 min [Fig. 1(f)–(h)] from bright and diffuse streaks to distinct and large spots corresponding to a transmission diffraction pattern that is characteristic for epitaxially grown islands [10,11]. Weak-intensity streaks appeared between the spots after 5–10 min [Fig. 1(j)–(l)] indicating a smoother surface. The transmission spots also decreased in size indicating a transition to larger crystallite domains due to the inverse relation between spot size and average crystallite size within the lateral coherence length of the electron beam (≈100 nm) [10]. These weak RHEED streaks became brighter and more pronounced after 10–20 min [Fig. 1(n)–(p)] while the size and intensity of the spots decreased. Modulated streaks could be observed after 20 min growth. This pattern indicates an unordered multilevel step surface [10]. For the untreated samples, the initial diffuse streaks changed into very weak-intensity and diffuse transmission spots connected with diffuse streaks after 4–5 min [Fig. 1(e)]. These spots were difficult to observe after 10 min while the diffuse streaks remained until the end of the growth [Fig. 1(i)–(m)].

Fig. 2 shows AFM micrographs of the sample surfaces after 5 [Fig. 2(a)–(d)] and 20 min [Fig. 2(e)–(h)] of ZnO deposition on untreated as well as on Zn, N and Ga pre-exposed GaN/Al_2O_3 templates.

The step-morphology of the underlying GaN-template is still clearly visible on the sample with an untreated GaN template surface [Fig. 2(a) and (e)] even after 20 min of growth. A low density (number of islands per unit area) of randomly dispersed islands can be observed on this sample. After 5 min growth the islands were 20–50 nm wide and 1.2–1.5 nm high. After 20 min growth the dispersed islands on the GaN-template were 15–30 nm wide and 0.5–0.7 nm high [Fig. 2(e)]. No coalescence of the islands had occurred on the untreated GaN.

On the surface of the Zn pre-exposed GaN, we observed ZnO islands that were 20–60 nm wide and 0.5–2.3 nm high after 5 min of growth [Fig. 2(b)]. The GaN template surface was still visible after 5 min of growth. After 20 min of growth, the ZnO islands had coalesced into a columnar film on the Zn pre-exposed GaN surface. The columns were 100–200 nm wide and 3–15 nm high [Fig. 2(f)]. The GaN template surface was not visible. Growth had clearly occurred after 20 min in contrast to the untreated case.

The samples with N pre-exposed templates exhibit islands that were 10–60 nm wide and 0.5–4.0 nm high [Fig. 2(c)]. The size of these islands were on average larger on the N pre-exposed GaN surface than on the Zn pre-exposed surface. The GaN template surface was not visible. Growth had clearly occurred after 5 min in contrast to the untreated case.

After 20 min a columnar film had also formed on the N pre-exposed GaN but here the columns or plateaus were both wider (150–550 nm) and higher (10–15 nm) [Fig. 2(g)]. The top surfaces of these plateaus were smooth with a peak-to-valley height difference of 0.5 nm. On the surface of the Ga pre-exposed GaN, we observed ZnO islands that were 20–300 nm wide and 1.0–1.5 nm high after 5 min of growth [Fig. 2(d)]. A columnar film had formed after 20 min [Fig. 2(h)]. The columns were irregular and were 100–200 nm wide and 10–20 nm high similar to the morphology observed on the Zn pre-exposed GaN template. The surface morphologies revealed by the AFM scans agree with the observed RHEED patterns. All samples with pre-exposed/pre-treated GaN template surfaces exhibited an unordered multilevel surface morphology that resulted in the observed modulated streaks at the end of the growths.

Fig. 3 shows SEM images obtained from the surfaces of the Ga pre-exposed GaN/Al_2O_3 templates with varying ZnO deposition times. Small-scale features can be observed already after 2 min [Fig. 3(a)]. After 5 min of ZnO growth, the surface exhibited 10–20 nm wide ZnO islands [Fig. 3(b)]. A columnar or grain-like surface morphology could be observed after 20 and 60 min growth [Fig. 3(c) and (d), respectively]. In contrast, it was not possible to discern any features in the SEM image of the surface of an as-received GaN template (not shown here).

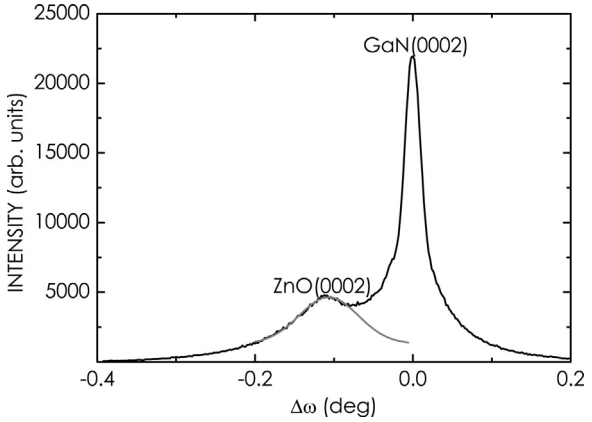

Fig. 5. X-ray rocking curve across the (0002) reflection from a ZnO(0001) layer grown on a GaN/4H-SiC(0001) buffer layer. We estimate the FWHM (gray line) of the ZnO peak to 389 arcsec. The FWHM of the GaN peak is 108 arcsec. The surface of the GaN/4H-SiC(0001) buffer layer was not exposed to air before the ZnO growth.

ToF-SIMS analysis was performed using an IONTOF TOF-SIMS V instrument equipped with a 25 keV Bismuth LMIG in the burst alignment mode (mass resolution m/Δm = 300; focus of the ion beam = 250 nm) using Bi_3^+ and Bi_3^{2+} ions with a target currents of 0.3 pA and 0.25 pA respectively. The burst alignment mode [12] is associated with a lower mass resolution and broader peaks but with a higher lateral resolution. Fig. 4(a) and (d) shows TOF-SIMS images obtained over an area of $10\times10\ \mu m^2$ from the surface of ZnO layers grown for 2 min on Ga pre-exposed GaN/Al_2O_3 templates exposed with the primary ion dose $Bi_3^{2+} = 1.02\times10^{14}$ ions/cm^2. An equal number of counts of ZnO^+ and Zn^+ ions were registered from the 2 min sample from a layer which is very thin. The corresponding surface after 5 min of growth is shown in Fig. 4(b) and (e) where the primary ion dose was $Bi_3^{2+} = 9.2\times10^{13}$ ions/cm^2. Here, the higher number of counts reflects a thicker ZnO layer. Images captured with the primary ion dose $Bi_3^+ = 2.45\times10^{14}$ ions/cm^2 of a ZnO nucleation layer grown for 5 min on Zn pre-exposed GaN templates [Fig. 4(c) and (f)] shows the existence of Zn^+ and ZnO^+ on this surface as well but cannot be directly compared with the previous images due to the higher ion dose. Fig. 4(g) shows the mass spectra for the ZnO layer grown for 5 min on Ga pre-exposed GaN/Al_2O_3 templates corresponding to [Fig. 4(b) and (e)].

Fig. 5 shows an X-ray rocking curve (XRC) across the symmetric (0002) reflection for a ZnO(0001) layer grown on a GaN/4H-SiC(0001) buffer layer. We estimated the full-width-at-half-maximum (FWHM) of the ZnO peak to 389 arcsec. The FWHM of the GaN peak was 108 arcsec. The 210–230 nm thick GaN layer was grown in the same system as the ZnO layers and immediately before starting the ZnO growth. This GaN film was never exposed to the ambient and therefore no sub-oxides could form on the GaN surface. No surface pre-treatment procedure was performed on the GaN buffer layer. Prior to starting the ZnO growth, the Zn shutter was opened for 1 min before turning on the O-plasma source in order to protect the GaN surface from O.

Fig. 6(a) shows an AFM micrograph and (b) a cross-sectional SEM image for the ZnO(0001) layer grown on GaN/4H-SiC(0001). The ZnO columns are 100–500 nm wide and 20–60 nm high [Fig. 6(a)]. The ZnO-layer thickness is measured to 115–175 nm [Fig. 6(b)]. Long, bright and sharp streaks were observed during the growth of the GaN/4H-SiC layer. Diffuse streaks were observed during the first

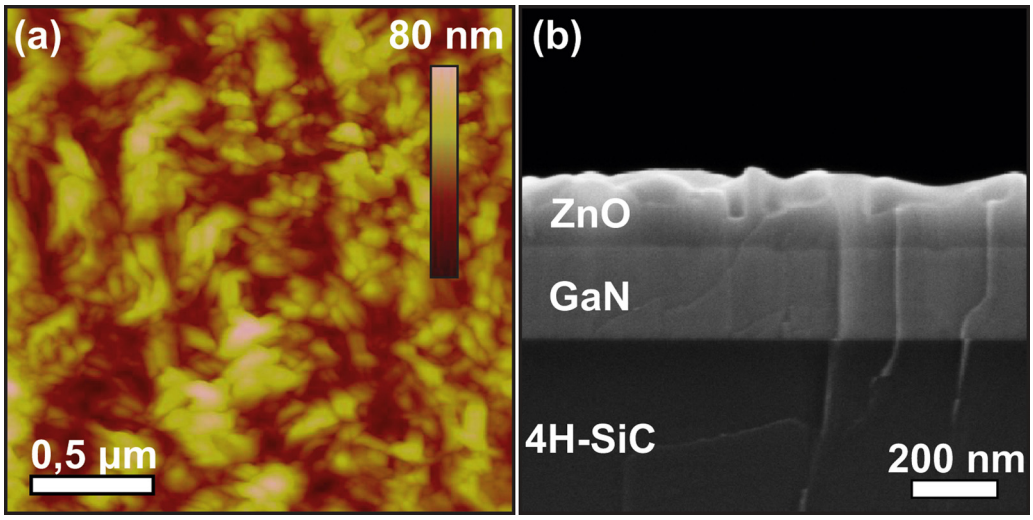

Fig. 6. AFM micrograph of a ZnO(0001) layer grown on a GaN/4H-SiC(0001) buffer (a). Cross-sectional SEM image of the ZnO/GaN/4H-SiC structure (b). The surface of the GaN/4H-SiC(0001) buffer layer was not exposed to air before the ZnO growth.

3 min of ZnO growth. Large and bright spots were formed after 3 min. The spots developed into large and bright facets that remained throughout the growth. The final observed RHEED-pattern is consistent with the large scale roughness observed in [Fig. 6(a)].

4. Conclusion

We have investigated ZnO nucleation and growth on GaN(0001) templates that were pre-exposed to Zn, N, and Ga or left untreated. Samples were also grown on 4H-SiC(0001) using a 210–230 nm thick GaN buffer layer deposited in the same MBE system used for ZnO growth. These GaN buffer layers were never exposed to the ambient and thus never formed sub-oxides. In addition, we did not subject the GaN buffer layers to any pre-treatment procedure and the surface was never directly exposed to the O-plasma. A high density of ZnO islands was observed on all pre-exposed samples as well as on the GaN/4H-SiC layer at the initial stages of the growth. These ZnO islands coalesced into a columnar ZnO film as the growth progressed. The width and height of the columns varied depending on the type of pre-treatment procedure. In contrast, the ZnO nucleation islands did not coalesce into a film on the untreated GaN template surface. Our conclusion is therefore that it is crucial to use a procedure for removing the Ga_xO_y sub-oxides to achieve ZnO growth on GaN(0001)/Al_2O_3 templates. Further, no such procedure was needed to achieve ZnO growth on the in situ grown GaN/4H-SiC(0001).

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