Structure and composition of GaN(0001) A and B surfaces

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Homoepitaxial, GaN films on both *c*-plane surfaces of bulk GaN crystals were examined using reflection high-energy electron diffraction (RHEED). Differences in the RHEED pattern, time development of the RHEED intensity, and surface reconstructions were observed. The substrate surfaces were prepared either by mechanical polishing [GaN(0001)A] or by chemo-mechanically polishing [GaN(000$\bar{1}$)B]. Then films were grown by molecular beam epitaxy; Ga was provide by a Knudsen cell and nitrogen from NH_3. On the B surface, the Ga rich reconstructions reported by Smith and co-workers [Phys. Rev. Lett. **79**, 3934 (1997)] were observed. On the A surface, a (2 ×2) reconstruction was observed. Both reconstructions were much sharper than those seen on GaN films grown on sapphire. RHEED measurements of the specular intensity vs time showed that two different surface terminations could be maintained on the B surface, one of which is a stable, gallided surface, while the other is a nitrided surface, which is unstable in vacuum. If the nitrided surface is heated in vacuum it changes to the gallided surface in several minutes at 800 °C. Only one termination was detected on the A surface. The results are complemented by desorption mass spectroscopy measurements, and the resulting surfaces were then investigated using atomic force microscopy and scanning tunneling microscopy. We were able to distinguish the two surface terminations on the B surface, and a unique annealing process under NH_3 will be documented. Preliminary investigation of the A surface revealed decorated step edges. The results were compared to films grown on sapphire with different nucleation layers, which can be grown to yield either polarity. © *1999 American Institute of Physics.* [S0021-8979(99)04411-4]

I. INTRODUCTION

Since wurtzite GaN is not centrosymmetric there are two distinct {0001} planes. These planes, GaN(0001) and GaN(000$\bar{1}$), will have different structure, composition, and chemistry. These differences could impact growth kinetics and possibly the doping characteristics of GaN. Studying these differences on GaN films grown on sapphire present two main difficulties: first, dislocations could dominate observations of growth, and second, it is often difficult to obtain single domain material of either polarity. To avoid high dislocation densities and inversion domains we examined growth on the two {0001} surfaces of bulk GaN single crystals. We distinguish the two polarities using their reconstructions and examine their response to adsorption of Ga and nitrogen. Initial investigations of the resulting structures are presented.

Different polarity assignments were reviewed by Hellman.[1] We follow the convention that the [0001] direction is a vector from a Ga atom to a N atom in the bulk wurtzite lattice. Then in a model in which the unreconstructed bulk surface is terminated with the fewest dangling bonds, the GaN(0001) surface (or GaN(0001)A) would have a Ga face and the GaN(000$\bar{1}$) surface (or GaN(000$\bar{1}$)B) would have a nitrogen face. Of course these surfaces reconstruct, most likely according to the currently accepted models.[2]

In this article we report reflection high energy electron diffraction (RHEED) observations of unipolar films grown on bulk GaN{0001} and compare the results to GaN grown on sapphire. Atomic force microscopy (AFM), scanning tunneling microscopy (STM), and desorption mass spectroscopy (DMS) were used to relate the RHEED data to the structure and composition of the surface.

II. EXPERIMENT

Single-crystal bulk GaN platelets were used for our measurements, with the opposing *c*-plane faces corresponding to the two possible polarities. These substrates, approximately 5×5 mm in size, were grown in Ga solution at high nitrogen

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pressures.[3] One of the polar faces can be chemo-mechanically polished[4] utilizing KOH, resulting in an atomically smooth surface with a root mean square (rms) roughness on the order of half a lattice constant, where $c = 5.2$ Å. No suitable chemical method has been found yet to polish the opposite face to comparable quality, so instead only a fine mechanical polish was applied.[4] Polishing could produce a slight misorientation from the c plane. These bulk samples were cleaned by boiling them first in acetone and then in methanol at 65 °C before mounting them on a Mo sample holder. Two mounting methods were used: The samples were either coated on their back side with 2000 Å of Ti and then mounted without stress by mechanical means,[5] or by bonding to an Al_2O_3 wafer using a GaSn eutectic.

Prior to the experiments the samples were outgassed for several hours at 300 °C and 1 h at 500 °C in a Varian Gen II molecular beam epitaxy (MBE) chamber. The base pressure of the growth chamber, with cryoshrouds cold, was $< 3 \times 10^{-9}$ Torr. The samples were then ramped to a temperature of 800 °C under an NH_3 beam equivalent pressure (BEP) of 1.0×10^{-5} Torr, with the NH_3 background pressure being 1.6×10^{-7} Torr. For the RHEED experiments, an approximately 3000 Å buffer layer was grown under slightly excess Ga conditions[6] by using a Ga flux of 1.0 monolayer (ML)/s (equivalent to a flux of 1.1×10^{15} cm^{-2} s^{-1}). All of the chemo-mechanically polished samples used for AFM measurements were grown at a lower substrate temperature of around 700 °C and a Ga flux of 0.1 ML/s. Those conditions resulted in the lowest hillock density, therefore improving our ability to resolve features between hillocks by AFM.[7]

GaN films were also grown on Al_2O_3 for comparison, both with GaN and AlN nucleation layers. The detailed procedures for etching, cleaning, and sample mounting are published elsewhere.[6] Prior to growth the substrates were outgassed for several hours at 300 °C in the preparation chamber of the MBE system, followed by 1 h at 500 °C in the growth chamber. The NH_3 leak valve was set to produce a BEP of 1.0×10^{-5} Torr. Then the substrate temperature was ramped at 100°/min from 500 to 1000° C for surface nitridation.

Experiments were performed by using two types of nucleation layer, AlN and GaN. In the case of the GaN nucleation layer, the sapphire was nitrided for 15 min whereas 3 or 15 min was used for the AlN nucleation layer, as discussed later. The 250 Å AlN nucleation layer was grown at 1000 °C using an Al flux of 0.10 ML/s (equivalent to 1.2×10^{14} cm^{-2} s^{-1}). RHEED showed transmission features in the pattern during and after AlN growth. The Ga shutter was then opened to provide a flux of 1.0 ML/s and the sample temperature was ramped down to 800 °C at 100°/min. The Al shutter was closed during the ramp below 900 °C.

The GaN nucleation layer was grown by repeating a sequence consisting of condensing Ga on the substrate surface at 700 °C and subsequent annealing at 800 °C under NH_3 ten times. This was achieved by ramping the substrate temperature to 700 °C, in the presence of a NH_3 BEP of 1.0×10^{-5} Torr. The Ga shutter was then opened at 1.0 ML/s and the substrate kept at 700 °C for about 1 min, during
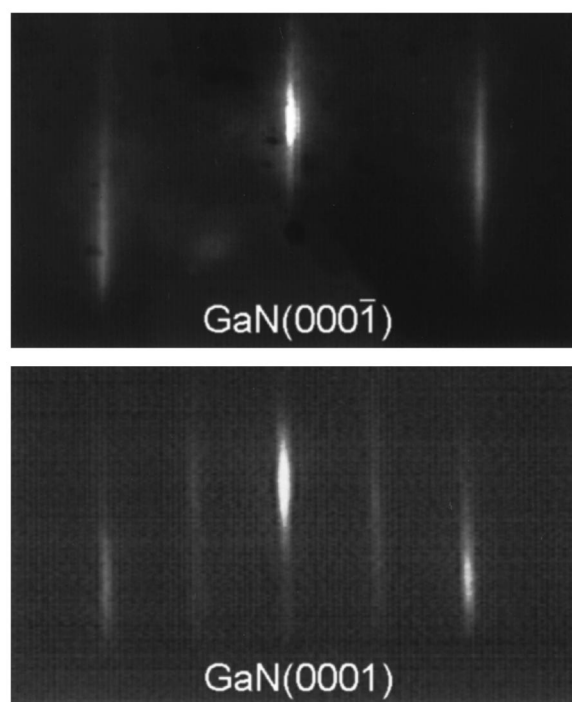

FIG. 1. RHEED pattern observed on bulk GaN along the $\langle 11\bar{2}0 \rangle$ direction for both polarities, under NH_3 after growth is stopped at about 800 °C.

which time the RHEED pattern completely disappeared. The Ga shutter was then closed and the sample ramped to 800 °C where it was kept for about 2 min until a RHEED pattern reappeared. This procedure was repeated ten times. Streaks were observed in the diffraction pattern after completion of this nucleation procedure.

Both types of nucleation layer were followed by a 2500 Å GaN buffer layer, deposited at 800 °C with a Ga flux of 1.0 ML/s and a NH_3 BEP of 1.0×10^{-5} Torr. After completion of the buffer layer, RHEED showed streaks without a transmission component. A (1×1) pattern was observed in the case of using GaN nucleation, while a weak (2×2) reconstruction was typically observed using AlN nucleation.

III. RESULTS

After growth of the buffer layer on the bulk crystals, as described earlier, the Ga flux was turned off and the RHEED patterns shown in Fig. 1 were observed. For these measurements the electron beam was along the $\langle 11\bar{2}0 \rangle$ direction and the NH_3 flux was held constant. The chemo-mechanically polished face exhibited a (1×1) pattern while the mechanically polished face was (2×2) reconstructed.[8] The streaks are elongated, even on these very smooth bulk samples, indicating the presence of atomic steps. The patterns are generally sharper than from the smoothest films of GaN that we have grown on sapphire.

To determine the crystalline polarity, we followed a procedure similar to that described by Smith *et al.*[9] Their method examines surface reconstructions with varying amounts of Ga on the surface. In our case, a chemo-mechanically polished surface was prepared as described earlier and then annealed in an NH_3 flux. Ga was then de-
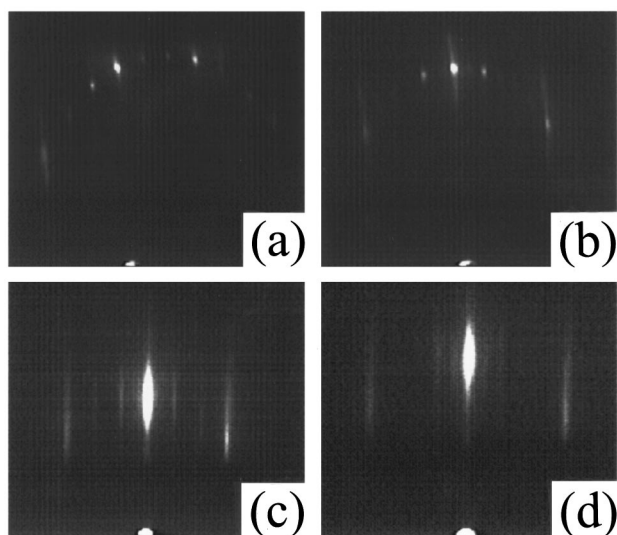
FIG. 2. Low temperature surface reconstructions observed on GaN(000$\bar{1}$)B, first reported by Smith *et al.* (Ref. 9) (a) (3×3) on bulk; (b) (6×6) on bulk; (c) (3×3) on Al$_2$O$_3$; and (d) (6×6) on Al$_2$O$_3$; The c(6×12) reconstructions are not shown; We found that these reconstructions are only observed on a Ga terminated (gallided) GaN(000$\bar{1}$)B surface.

FIG. 3. RHEED intensity behavior of both polarities at around 750 °C. (a) Two surface terminations were observed on GaN(000$\bar{1}$)B. (b) Only one surface termination was detected on GaN(0001)A, but a reconstruction transition between (2×2) and (1×1) is observed.

posited in the absence of NH$_3$ at a rate of 0.1 ML/s at about 700 °C for 1 min. The substrate temperature was then lowered to about 400 °C and an additional fractional ML of Ga was deposited. Depending on the amount of additional Ga deposited, and upon cooling to below 300 °C, various reconstructions could be observed. Figures 2(a) and 2(b) show the reconstructions observed on the chemo-mechanically polished face[8] along the $\langle 11\bar{2}0 \rangle$ direction. These are compared to those observed on sapphire, grown with a GaN nucleation layer, shown in Figs. 2(c) and 2(d).

The same procedure was followed on the mechanically polished face, but did not result in the observation of any reconstructions. In fact, the (2×2) reconstruction seen at typical growth temperatures disappears upon cooling the sample to 400 °C, resulting in a (1×1) RHEED pattern. The only effect of adding Ga was a weakening of the (1×1) pattern. Based on these observations we assign[8] the GaN(000$\bar{1}$)B polarity to the chemo-mechanically polished, bulk face, which is in agreement with convergent beam diffraction studies performed by Liliental-Weber *et al.*[10] and hemispherically scanned x-ray photoelectron diffraction studies by Seelmann-Eggebert *et al.*[11]

In order to extract more information on the adsorption behavior of Ga, we monitored the specular RHEED intensity on both polarities along the $\langle 11\bar{2}0 \rangle$ beam direction, shown in Fig. 3. Note that these measurements were taken at a typical growth temperature around 750 °C, significantly above the temperature required to observe the low temperature reconstructions on GaN(000$\bar{1}$)B. The behavior of the specular intensity, upon opening and closing the Ga shutter, is very different on the two surfaces.

On GaN(000$\bar{1}$)B, shown in Fig. 3(a), we start with a surface that had been annealed in NH$_3$; then all fluxes were removed. Exposing the surface to a Ga flux causes the dif-
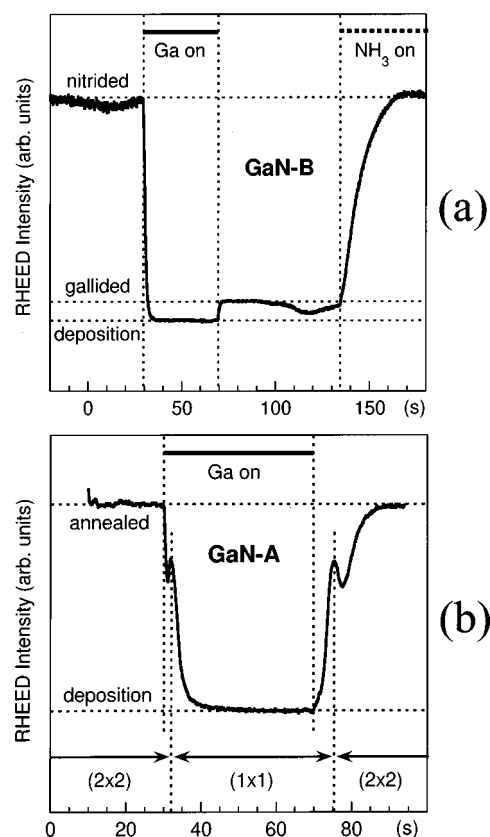
fracted intensity to drop to a new steady state value that depends on the magnitude of the Ga flux and the substrate temperature. When the Ga flux is interrupted, a fractional ML of Ga desorbs, as measured by DMS,[5] and the intensity rises to a slightly higher value. This last value of the diffracted intensity will remain indefinitely and is independent of temperature. In this sense this gallided surface is stable and neither a flux of N nor Ga need be supplied in order to maintain it. If a NH$_3$ flux is then reintroduced and the surface nitrided, the diffracted intensity returns to its initial value. This nitrided surface can be maintained at this relatively low temperature without incident fluxes for some time; however, as shown later, it ultimately goes to the previous, stable, gallided surface.

In order to better understand the adsorption of Ga on both a nitrided and a gallided GaN(000$\bar{1}$)B surface, we recorded the transient Ga adsorption behavior with DMS from both surfaces, which are shown in Fig. 4(a) as superimposed curves. The first curve was obtained from a GaN(000$\bar{1}$)B surface which was prepared by exposure to NH$_3$. Then NH$_3$ flux was removed, and the film exposed to Ga for approximately 1 min. The transient DMS signal upon opening the Ga shutter is recorded in Fig. 4(a) as one curve. The Ga shutter was then closed for approximately 1 min. Then reopened again, plotted as a superimposed curve in Fig. 4(a). Comparing both curves we see that the nitrided surface adsorbs more Ga than the gallided surface, apparent from the
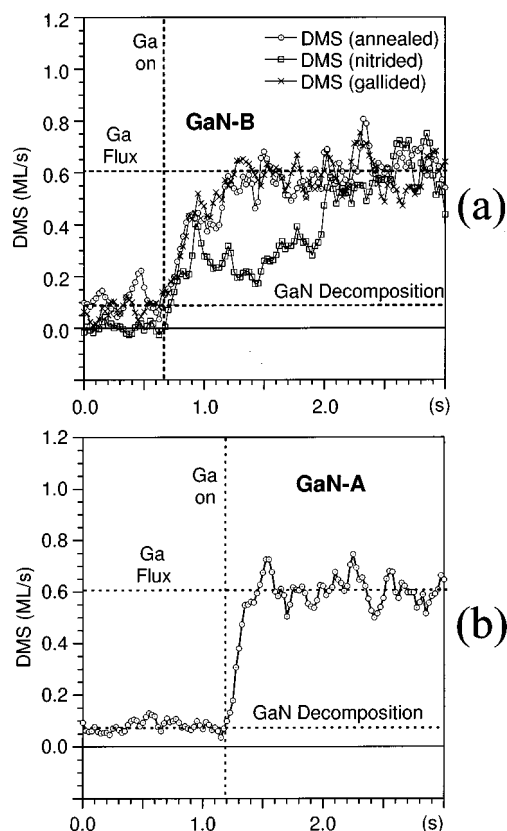
FIG. 4. Transient DMS measurements of GaN grown on sapphire upon opening the Ga shutter at 0.61 ML/s at a substrate temperature of 813 °C. (a) superposition of three Ga adsorption measurements on a GaN(000$\bar{1}$)B surface which was nitrided, then gallided, and finally nitrided followed by annealing in vacuum; and (b) GaN(0001)A surface which resulted in similar curves regardless of sample history.

FIG. 5. RHEED and DMS signal during annealing of a nitrided GaN(000$\bar{1}$)B surface, showing the change from a nitrided to the gallided surface (Ga flux=0.61 ML/s, T=823 °C). The inset is an Arrhenius plot of the time required to go from a nitrided to a gallided surface over the temperature range from 790 to 870 °C. It shows an activation energy of 4.4 eV.

reduced Ga desorption on the nitrided surface in comparison to the gallided surface. We also note that the Ga adsorbed on a previously gallided surface is identical to the amount desorbed after the shutter is closed, which is not shown in the figure. We therefore conclude that the nitrided surface adsorbs Ga strongly, and once gallided it adsorbs Ga only weakly. This says that the nature of the adsorption sites on GaN(000$\bar{1}$)B depends on how the surface has been prepared.

We stated before that the nitride surface is unstable in vacuum, and that it will ultimately convert to the gallided surface. Evidence for such process is shown in Fig. 4(a) as another superimposed curve, where the same Ga adsorption experiment was performed after annealing a previously nitrided film for a long time in vacuum. As seen from the transient response, this annealed surface behaves like the gallided surface, and does not adsorb any additional Ga like the nitrided surface. In comparison, the GaN(0001)A surface gave similar adsorption results regardless of sample history, i.e., after exposure to Ga or NH$_3$ only, and after vacuum annealing. A sample curve is shown in Fig. 4(b), which looks very similar to the curve from the gallided GaN(000$\bar{1}$)B surface. We note that all of the adsorbed Ga was desorbed again after closing the Ga shutter. This result suggests that the GaN(0001)A surface structure is the same in vacuum after
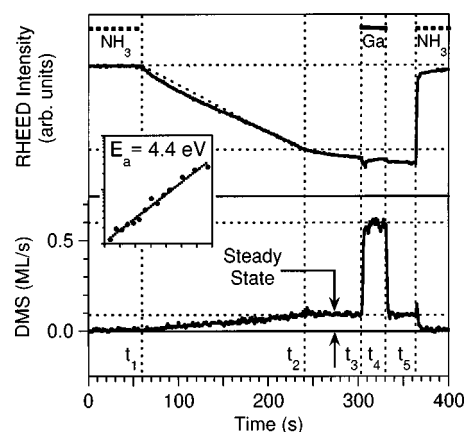
Ga or NH$_3$ exposure, very different from the GaN(000$\bar{1}$)B surface.

We investigated the annealing behavior of the nitrided GaN(000$\bar{1}$)B surface in more detail. Both the RHEED intensity, as well as the Ga DMS signal were monitored during annealing, which is plotted versus time in Fig. 5. Initially the sample is kept under ammonia, and a steady state RHEED intensity is recorded during that time along with no detectable Ga signal by DMS. At t_1 the ammonia flux is turned off, and an approximately linear decrease of the RHEED signal is recorded between t_1 and t_2, accompanied by an approximately linear increase in the DMS signal. At t_2 a steady state is reached, with perhaps a slight decrease in the RHEED signal due to surface roughening. Between t_3 and t_4 the sample was exposed to a Ga flux, but there is no detectable change before and after exposure, both for RHEED and DMS. At t_5 the ammonia is turned back on, after which the RHEED intensity recovers to its original value and the DMS signal reduces again below the detection limit. The annealing process between t_1 and t_2 was found to be temperature activated. The activation energy was found to be 4.4 eV as plotted in the insert of Fig. 5. If our interpretation is correct that the nitrided surface anneals to the gallided surface during decomposition in vacuum, we would expect the decomposition rate after annealing to equal the decomposition rate obtained after galliding a nitrided surface before annealing. This results, not shown, was in fact obtained. Therefore, we conclude that a nitrided surface is unstable in vacuum, annealing to a stable gallided surface via a temperature activated process with E_a=4.4 eV. This process was found to take on the order of minutes even at temperatures as high as 800 °C.

By comparison, on the GaN(0001)A polarity shown in Fig. 3(b), the diffracted intensity also decreases when Ga is adsorbed. But here, once the Ga flux is removed, the diffracted intensity returns to its original value. The change in intensity with time is not monotonic, which we correlated to a reconstruction change between (2×2) and (1×1). At this

temperature, we cannot add any amount of Ga that will remain in the absence of a Ga flux, as discussed earlier in Fig. 4(b). At sufficiently high Ga fluxes the (2×2) reconstruction changes to a (1×1) RHEED pattern. This (1×1) pattern returns back to (2×2) once the Ga shutter is closed, even in the absence of NH_3. The initial and final RHEED intensities were found to be independent of NH_3 flux. Thus, in contrast to the GaN$(000\bar{1})$B surface, we can not change the steady state surface coverage of Ga on the GaN(0001)A surface. Excess Ga cannot be maintained at typical growth temperatures without an incident Ga flux.

At these high growth temperatures surface processes such as desorption and diffusion are quite rapid, suggesting that the growth front and the annealed surface could be quite different. To examine this possibility, to some extent guided by the variation in the RHEED intensity data shown in Fig. 3(a), we examined the morphology of the GaN$(000\bar{1})$B surface vs the rate at which growth was interrupted. GaN films were grown for 3 h under the conditions described earlier, followed by different cooling procedures. The NH_3 flux was held fixed since it could not be interrupted easily. The results of those experiments are shown in the series of AFM images in Fig. 6, which all show macrosteps, but with different structures on the step terraces.[12]

Specifically, Fig. 6(a) shows a sample that was annealed after growth for several minutes under NH_3 before cooling, which resulted in terraces covered with irregularly shaped islands on the order of 500 Å across and 2–5 Å in height. Figure 6(b) shows a sample that was cooled down slowly, at a rate of roughly 100° per min. Areas with similar islands are observed, but only in regions starting at a descending step edge. Apart from this island region, the rest of the surface appears to be featureless. The width of these regions was approximately equal, each roughly 350 Å. Finally, the sample shown in Fig. 6(c), was quenched rapidly after the Ga shutter was closed. These last data were obtained in a different MBE apparatus, with a base pressure of 1×10^{-10} Torr, but using otherwise similar growth conditions. In this last case, all terraces appear to be featureless, except for a few small steps between the macrosteps. The height of these steps was approximately half a lattice constant $c/2$. The width of the island regions originating from descending step edges depends on annealing time (or quenching rate) under NH_3, while the remainder of the surface is unchanged.

We note that the featureless terraces are also obtained when an annealed or partially quenched surface is exposed to Ga in the absence of NH_3, which shows that NH_3 is required in order for the surface transformation illustrated in Fig. 6 to occur. Further, gallided films were annealed in NH_3 while monitoring the RHEED intensity recovery like in Fig. 3, with the difference that the samples were quenched in the early stages of this recovery. Subsequent AFM scans resulted in films similar to Fig. 6(b), which showed partial nitridation originating from the descending step edges. These results clearly show that the change in RHEED intensity during annealing in NH_3 originates from the development of the island zones on the sample surface.

Monatomic steps, instead of the macrosteps of Fig. 6, could sometimes be observed as shown in Fig. 7. Figure 7(a)
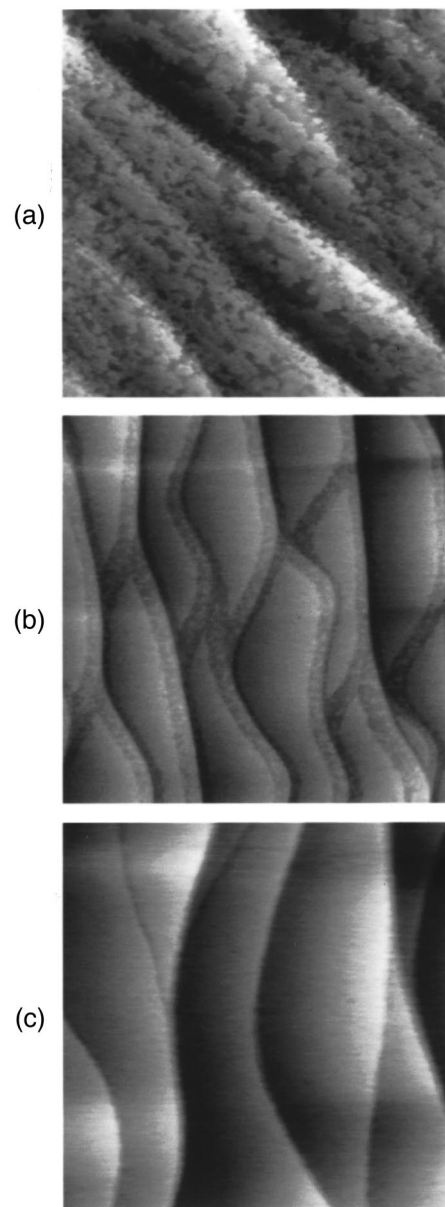

FIG. 6. Three 1×1 μm AFM scans of the GaN$(000\bar{1})$B surface with macrosteps cooled at different rates under NH_3 after growth was interrupted at 725 °C. (a) annealed, then cooled; (b) slowly cooled; and (c) quenched. Note that the same featureless surface as in (c) is obtained after Ga only exposure in the absence of NH_3.

shows a 500×500 nm STM scan, and $c/2$ steps on the order of 200 Å. A zoom is shown in Fig. 7(b). This film was annealed in ammonia and then cooled to room temperature before STM. At the higher magnification in Fig. 7(b) one can see line defects perpendicular to the step edges.

Comparing GaN films grown on sapphire to bulk GaN, we found that films grown with our GaN initiation layer on sapphire exhibit a (1×1) RHEED pattern and low temperature reconstructions. On the other hand, GaN films grown with our AlN initiation layer on sapphire behaved differently. Films which were nitrided for 15 min typically featured a very weak (2×2) reconstruction, as well as very weak low temperature reconstructions. Films nitrided for 3 min showed a much stronger (2×2) reconstruction, and the low temperature reconstructions were absent.
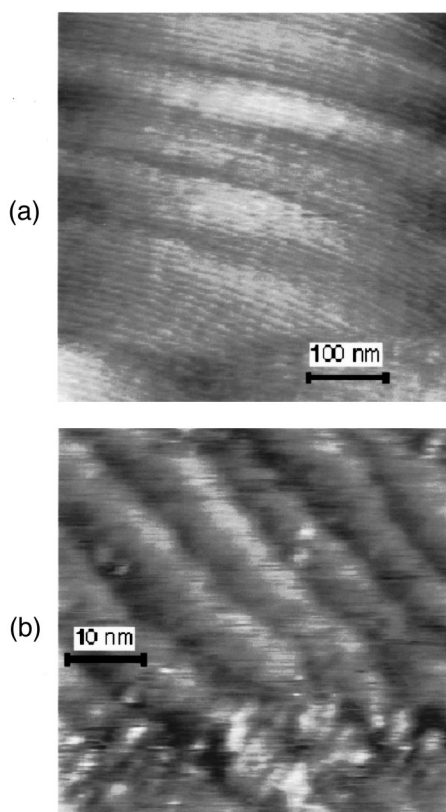
FIG. 7. Monatomic steps on a GaN(000$\bar{1}$)B surface. (a) 500×500 nm STM scan; and (b) 50×50 nm STM scan.
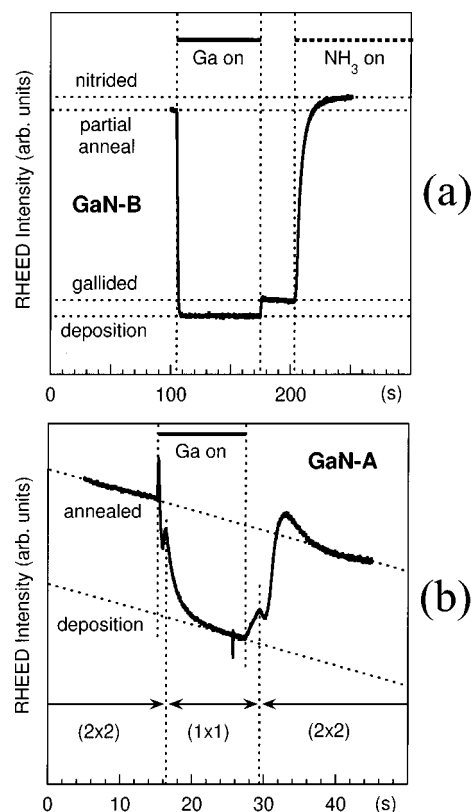

FIG. 8. RHEED intensity behavior of GaN grown on sapphire at around 750 °C, with: (a) GaN nucleation layer (Ga flux at 0.6 ML/s); and (b) 3 min nitridation and AlN nucleation layer (Ga flux at 0.1 ML/s).

The time dependence of the RHEED intensity for these films is shown in Fig. 8. The film with the GaN nucleation layer behaved like the chemo-mechanically polished GaN(000$\bar{1}$)B bulk face. The film with the AlN nucleation layer which was nitrided 3 min was similar to the mechanically polished GaN(0001)A bulk face. The data shown in Fig. 8(b) shows a behavior similar to that of Fig. 3(b), but is superimposed on top of a linearly decreasing background, suggesting surface roughening, as indicated by the dashed lines. At these temperatures there is an increase in the desorbed Ga DMS signal, suggesting that the increased roughness is due to decomposition of the highly defected GaN on Al$_2$O$_3$. Finally, in Fig. 8(b) one can also clearly see an intermediate maximum when there is a transition between (2×2) and (1×1) reconstructions. This transition occurs when about 1/2 ML of Ga is added or desorbed, as determined from the known incident flux and DMS calibration. In short, these RHEED measurements from GaN/sapphire films give nearly identical results to those of much smoother bulk surfaces. This means that in both cases the step edges and non-{0001} faces do not play a significant role in the RHEED data. Further, since the two polarities give very similar results to the single domain bulk crystals, and since the low incident angle RHEED beam samples a large stripe on the surface, these data suggest that in both cases, using the nucleation procedures noted, we have essentially single domain films.

The earlier films were etched in KOH[11,2] in order to distinguish between polarities and check whether there are indeed no inversion domains. Etching is expect to occur for defects, including GaN(000$\bar{1}$)B inversion domains. We find that there was significant etching for films with a GaN nucleation layer, while no detectable etching took place for the film with the AlN nucleation layer which was nitrided for 3 min. The film that was nitrided for 15 min before depositing the AlN nucleation layer showed etched and unetched regions, indicative of defects and inversion domains. For the unetchable film the density of inversion domains was found to be less than 5%, which places a limit on the RHEED method to detect inversion domains.

Due to the surface roughness of the bulk GaN(0001)A samples, we did not do an extensive series of AFM measurements. Figures 9(a)–9(c) are AFM images of the mechanically polished surface, at various magnifications, after 3 h of growth at approximately 800 °C, a Ga flux of 1.3 ML/s, and a NH$_3$ BEP of 1.0×10^{-5}. The surface is quite rough, consisting of flat topped posts, typically around 2500 Å across. Steps can be seen on top of these posts with terraces that are about 250 Å wide. Further, the step edges and post edges appear to be decorated, as evident from elevated lines at those locations. We were unable to measure the exact height of the steps since both the steps and the decorations are on the order of only a few Å. The grooves in Fig. 9(a) must be remnants of the polishing procedure, and to some extent the flat-topped posts follow these lines.

IV. DISCUSSION

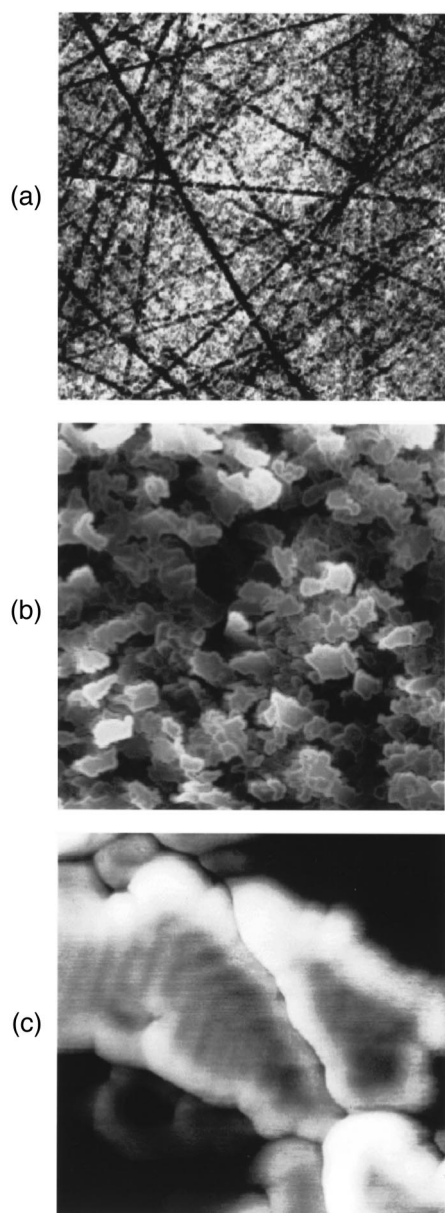We have shown that GaN(0001)A and GaN(000$\bar{1}$)B differ significantly in their adsorption behavior of Ga and NH$_3$.

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FIG. 9. AFM images from a GaN(0001)A surface after 3 h of growth at about 800 °C with a Ga flux of 1.3 ML/s and a NH_3 BEP of 1 $\times 10^{-5}$ Torr. (a) Grooves left from the mechanical polishing process (50 $\times 50$ μm, $z = 150$ nm); (b) Posts of different height with raised perimeters (5$\times 5$ μm, $z = 90$ nm); and (c) Atomic steps on top of posts with raised step edges (500$\times 500$ nm, $z = 30$ nm).

In particular, we presented data that showed that GaN(000$\bar{1}$)B has at least two types of adsorption sites. One type exists on a nitrided surface and permits Ga to bond strongly. If a surface is exposed to a sufficient amount of Ga these strongly bonding sites are replaced by weak bonding sites. This gallided surface allows the addition of weakly bound Ga that desorbs quickly once the Ga flux is removed. In contrast to the GaN(000$\bar{1}$)B surface, the GaN(0001)A surface adsorbs Ga only weakly, independent of sample history, i.e., previous exposure to Ga, ammonia, or annealing in vacuum.

During growth on the GaN(0001)A surface both a (1 $\times 1$) and (2$\times 2$) RHEED pattern could be observed. This

reconstruction change was found to depend on the Ga to NH_3 flux ratio. Hacke *et al.*[13] investigated this transition as a function of growth parameters. Since they observed the same reconstruction change we saw, we conclude their films were GaN(0001)A films. They found that the transition is temperature activated with an activation energy of about 2.76 eV. This activation energy is close to the activation energy of Ga over liquid Ga, consistent with our results that GaN(0001)A has only one weak adsorbing site.

Since the GaN(0001)A surface structure is the same in vacuum, during NH_3 exposure, and after NH_3 or Ga exposure, the question arises how the weakly adsorbed Ga participates in the growth process. We note that we did not observe RHEED intensity oscillations[6] on GaN(0001)A. Further, in Fig. 4 we saw that unlike for GaN(000$\bar{1}$)B, we could not measure any significant amount of Ga adsorption on GaN(0001)A after NH_3 exposure. Ga adsorbs only if there is a coincident NH_3 flux. Therefore, we conclude that growth does not occur by island nucleation on terraces, but rather by step flow.

GaN(0001)A films which were grown under the conditions indicated in Fig. 9 resulted in the RHEED pattern of Fig. 1. Since there are no transmission features seen in this RHEED pattern, the diffraction must be due to the flat surfaces on top of the posts in Fig. 9. These posts are typically 2500 Å in diameter and so the incident beam cannot be transmitted through them. Further, we note that there are steps on top of the posts that are seen to intersect with angles of 120° between them. The steps on top of the posts, as well as the post edges, feature raised lines, suggesting decoration by Ga atoms due to a step-edge barrier on GaN(0001)A.

In conjunction with the STM measurements conducted by Smith *et al.*,[2] we can draw a clear picture of the two GaN(000$\bar{1}$)B surfaces which provide the two different types of adsorption sites. Exposure to NH_3 results in the nitrided surface structure. Although this structure is unstable in vacuum, it can be maintained for a long time depending on sample temperature, as shown earlier in Fig. 5. This nitrided surface, which was prepared in Fig. 6(a), is characterized by islands on top of otherwise flat terraces between steps. Note that there seem to be fewer islands very close to step edges. When exposing this nitrided GaN(000$\bar{1}$)B surface to a Ga flux in the absence of NH_3, the surface becomes essentially featureless between steps, as presented in Fig. 6(c). DMS measurements showed that Ga strongly bonds onto that surface until the surface is covered by 1 ML of Ga.[14] Any additional Ga weakly bonds on top of the strongly adsorbed Ga and desorbs quickly after the Ga shutter is closed. If the substrate temperature is lowered below 300 °C, the reconstructions reported by Smith *et al.*[9] are observed, provided additional weak adsorbing Ga (less than 1 ML) is added at a temperature low enough to prevent desorption. Note that it is essential to first gallide the surface in order to observe these reconstructions. Above 300 °C these reconstructions disappear, but reappear once the temperature is lowered again below 300 °C. Smith *et al.* argued that this reversible transition represents an order/disorder transition; hence, at these low temperatures no significant amount of this fractional

weak bound Ga layer is desorbed, in agreement with our result that this weakly adsorbed Ga is well described by the adsorption of Ga on liquid Ga,[5,6] which at this temperature is below the detection limit of our DMS.

The gallided surface is nitrided by exposure to NH_3. We showed in the AFM scans of Fig. 6 that this nitridation process proceeds from descending step edges. The nitrided surface has been shown to contain both N and H.[15] On relatively flat areas between macrosteps, we observed the small islands of Fig. 6(a) on an otherwise smooth surface. These islands, which are big enough to be resolved laterally by AFM, appear to be irregularly shaped, different from those reported by Xie *et al.*[16] Those islands were triangular pointing in two different directions. When looking at the bonding arrangements of a strongly adsorbed Ga island vs a GaN island on a GaN(000$\bar{1}$)B surface, we notice that GaN islands have two possible sides with different bonding arrangements, while strong adsorbing Ga according to the model of Smith *et al.*[9] does not. Assuming that one of the GaN Island bonding arrangements is more stable than the other, we could expect such islands to be triangular in shape. Since the islands we observe are of irregular shape we believe that they are strong binding Ga islands. This conclusion is supported by DMS measurements to be published elsewhere,[14] which show that somewhat less than a ML of Ga is needed to complete the ML of strong binding Ga.

We presented AFM and STM results in Figs. 6 and 7 that showed both macrosteps and monatomic steps on GaN(000$\bar{1}$)B samples grown under similar conditions, and regions with both types of steps were observed even on the same sample. At this point the origin of the different types of steps is unclear. We do not yet know if the macrosteps are the final development of the step bunching observed in Fig. 7. Another possibility for the formation of the macrosteps might be the nature of the nucleation process, depending on slight differences in sample preparation resulting in impurities or defects on the surface, permitting preferential growth at certain defect sites.

Samples with monatomic steps were shown in the STM image of Fig. 7. After annealing in NH_3, line defects can be seen that run parallel to each other, perpendicular to the step edges. Packard *et al.*[17] reported a similar structure after annealing metalorganic chemical vapor deposition samples in vacuum at 900 °C for several minutes. According to our results, this procedure would have either led to the gallided GaN(000$\bar{1}$)B surface, or kept a GaN(0001)A surface unchanged, ignoring GaN decomposition. We should note that Smith *et al.*[9,2] did not observe any similar defects on their gallided GaN(000$\bar{1}$)B surfaces, nor on the GaN(0001)A surface. Based on those results we are unable to match Packard's[17] observations with ours.

V. CONCLUSION

GaN was grown on both c-plane surfaces of bulk GaN using MBE with NH_3. Due to their unipolar nature, the availability of bulk GaN platelets permitted us to unambiguously compare the adsorption behavior of Ga and NH_3 on both GaN{0001} polarities. RHEED was used to distinguish both polarities and to investigate different surface structures on those polarities, which we related to the transient Ga adsorption as measured by DMS. These surface structures were then imaged by AFM and STM. From the observed surface reconstructions, the face that could be chemo-mechanically polished was assigned to the GaN(000$\bar{1}$)B surface, and the face that can only be mechanically polished to the GaN(0001)A surface. After growth on the GaN(000$\bar{1}$)B surface, $c/2$ steps, as well as macrosteps 15–20 Å high were observed. Two different GaN(000$\bar{1}$)B surface terminations could be prepared by exposing the surface to either Ga or NH_3 only. The gallided surface was found to be the stable surface termination after annealing in vacuum. The gallided surface is essentially featureless between steps, while the nitrided surface exhibits an island structure. This island structure is initiated at the upper terrace of a step edge during annealing in NH_3. The GaN(0001)A surface showed residual polishing damage and a post-like surface morphology with decorated step edges. Only one stable surface termination was found after growth above 700 °C. Since we are now able to determine the polarity of GaN films by RHEED, we applied these techniques to GaN films grown on sapphire. We developed two different nucleation procedures yielding unipolar films of either polarity.

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