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Y. Dong
Carnegie Mellon University

R. M. Feenstra
Carnegie Mellon University, feenstra@cmu.edu

D. W. Greve
Carnegie Mellon University

See next page for additional authors

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Authors
Y. Dong, R. M. Feenstra, D. W. Greve, J. C. Moore, M. D. Sievert, and A. A. Baski

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Effects of hydrogen on the morphology and electrical properties of GaN grown by plasma-assisted molecular-beam epitaxy

Y. Dong and R. M. Feenstra[a)]
Department of Physics, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

D. W. Greve
Department of Electrical and Computer Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

J. C. Moore, M. D. Sievert, and A. A. Baski
Department of Physics, Virginia Commonwealth University, Richmond, Virginia 23284

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We study the effect of introducing hydrogen gas through the rf-plasma source during plasma-assisted molecular-beam epitaxy of GaN(0001). The well-known smooth-to-rough transition that occurs for this surface as a function of decreasing Ga flux in the absence of H is found to persist even with H present, although the critical Ga flux for this transition increases. Under Ga-rich conditions, the presence of hydrogen is found to induce step bunching (facetting) on the surface. Conductive atomic force microscopy reveals that leakage current through dislocation cores is significantly reduced when hydrogen is present during the growth. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1890482]

The basic growth techniques for GaN films can be divided between those in which abundant hydrogen is present [e.g., metalorganic chemical vapor deposition (MOCVD)[1] and reactive molecular beam epitaxy (RMBE) using ammonia[2]] and those without intentionally introduced hydrogen [e.g., plasma-assisted MBE (PAMBE)[3]]. The surface structures of GaN films grown by PAMBE are quite well understood due to the relative ease in carrying out *in situ* surface studies. The main surface structure of Ga-polar (0001) films grown under Ga-rich conditions consists of about 2 monolayers (1 bilayer) of Ga on the surface, i.e., the "1×1" surface.[3] In the presence of H, $(1\bar{1}01)$ surface facets have been observed.[4] Studies have been carried out focusing on the growth rate dependence of GaN films of both polarities in the presence of H.[5,6] Theoretical work has been performed to investigate the effect of H on GaN growth.[7,8] In this work, we study the GaN(0001) surface structure in the presence of H, in an effort to better understand differences between various growth techniques.

For PAMBE in the absence of H, it is well known that a smooth-to-rough transition occurs when the Ga-flux is reduced, during which the surface structure changes from the Ga-rich "1×1" to a Ga-poor surface terminated by Ga or N adatoms.[3] We find in the present work that, for relatively low pressures of H, this transition persists but the critical Ga flux at which it occurs increases as the H pressure increases. Under Ga-rich conditions with the "1×1" present, the effect of hydrogen is to modify the surface morphology: step bunching and facetting is observed. Subsequent annealing of this step-bunched surface produces small surface depressions, similar to those commonly reported for MOCVD-grown GaN and associated with dislocations intersecting the surface.[1,9] Conductive atomic force microscopy reveals that the leakage current through the dislocation cores is significantly reduced when hydrogen is present during the growth. We argue that H selectively bonds to surface step and/or kink sites.

Our GaN growth is performed with a rf-plasma source of N at a fixed N_2 partial pressure of 2×10^{-5} Torr and using an effusion cell for Ga, in an ultrahigh vacuum growth chamber equipped with reflection high-energy electron diffraction (RHEED). Hydrogen gas (partial pressure varied from 2×10^{-8} to 2×10^{-6} Torr) is introduced through the rf-plasma source. The spectral line of atomic hydrogen is observed from optical spectra of the plasma suggesting that some of the H_2 molecules have dissociated, but the exact percentage is unknown. All growths discussed here were performed at 780 °C. Substrates consist of either H-etched 6H–SiC(0001) (Si-polar) wafers or commercially available GaN(0001) (Ga-polar) films on sapphire [grown by hydride vapor phase epitaxy (HVPE)], both without intentional miscut. We measure a rocking curve FWHM of the (0002) peak in x-ray diffraction for these HVPE GaN films of typically 420 arcsec, implying a screw or mixed threading dislocation density of about 1×10^9 cm^{-2}.[10] The surface morphology was studied using *ex situ* atomic force microscope (AFM), in contact mode, and microscopic current–voltage measurements were performed using conductive AFM (CAFM). Macroscopic Schottky diodes were formed with Ni/Au circular contacts with diameters of 180 or 360 μm, using indium as an ohmic contact.

The first observed effect of hydrogen is to shift the streaky-to-spotty transition point observed in RHEED. The Ga flux for this transition increases as the abundance of hydrogen increases, e.g., the transition Ga flux increases by 50% when the partial pressure of hydrogen increases from 2×10^{-9} to 2×10^{-6} Torr at a substrate temperature of 700 °C.[11] This result is consistent with observations of Van-Mil *et al.*,[6] who suggest that atomic nitrogen atoms are a relatively inefficient species for the growth of GaN.[6] In the presence of H, however, these species can be efficiently captured, perhaps by forming surface adsorbed species similar to those occurring during RMBE growth with ammonia

[a)]Electronic mail: feenstra@cmu.edu

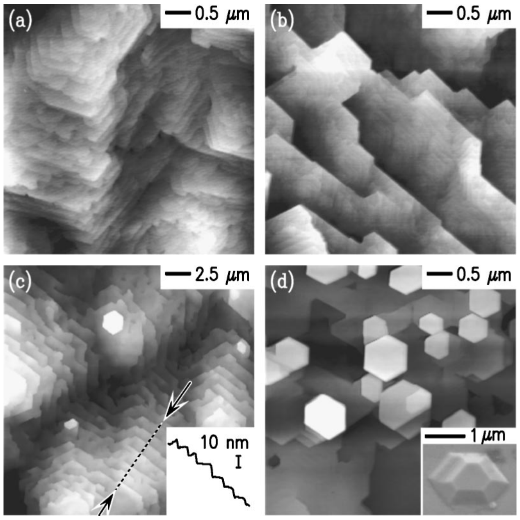

FIG. 1. (a) AFM image of GaN film grown with pure N_2 (gray scale 8 nm). (b), (c), and (d) AFM images of GaN films grown in the presence of H (gray scales 11, 46, and 41 nm, respectively). Line cut along the dashed line in (c) is shown in the inset. The inset in (d) is a scanning electron micrograph of a large hexagonal island on the surface. Films shown in (a)–(c) are grown on HVPE-GaN-on-sapphire substrates, whereas the film shown in (d) is grown on a H-etched SiC substrate.

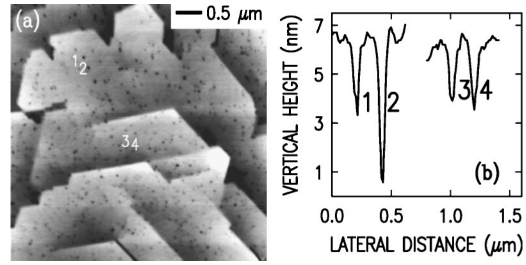

FIG. 2. (a) AFM image of a GaN film grown in the presence of H that has undergone an additional 3 min N_2+H_2 plasma exposure at 780 °C (gray scale 10 nm). (b) Line cuts of four surface depressions, with their identifying numbers (1–4) shown directly below each depression in (a).

(NH_3).[2] Thus, the presence of hydrogen is expected to increase the amount of active N species available for GaN growth. In this scenario, H does not affect the growth by bonding directly to the GaN surface, but rather, it modifies the gas phase kinetics and/or the surface adsorbed species. It should be emphasized that under Ga-rich conditions (streaky RHEED pattern), even with the presence of hydrogen, the surface termination of the (0001) surface is still "1×1," as determined by RHEED, Auger electron spectroscopy, and low energy electron diffraction. Only when the partial pressure of hydrogen reaches 2×10^{-6} Torr, with the substrate temperature lowered to 660 °C and under Ga-lean conditions do we observe a different RHEED pattern, namely a sharp 2×2.[11] The conditions in this case are similar to those predicted in Ref. 7 to produce a 2×2 arrangement arising from H adatoms on the surface.

Figures 1(b) and 1(c) show AFM images of a film grown in the presence of hydrogen (H_2 partial pressure of 2×10^{-6} Torr). Step bunching is clearly visible in these images and also in the line cut of Fig. 1(c). In contrast, a film grown without hydrogen, Fig. 1(a), does not display bunching. It should also be noted that within each terrace separated by the step bunches, small unit-cell high steps still occur. Typical step heights in Fig. 1(c) are found to be 6–12 nm, as compared to the unit cell height for GaN of 0.52 nm. Larger step bunches/facets are also observed, e.g., the hexagonal island in the upper half of Fig. 1(c), with a step height of 90 nm. Actually, the latter large-step-height bunches are more predominant on films grown on SiC [see Fig. 1(d)] whereas the 6–12 nm high bunches are observed on films grown on HVPE GaN [as in Figs. 1(b) and 1(c)]. The latter may be influenced by screw-type dislocations with a Burgers vector of this same magnitude, present in the HVPE-grown substrates. A scanning electron micrograph (SEM) of a hexagonal island having an especially large height is shown in the inset of Fig. 1(d). Due to its large height, sidewall facets are clearly visible for this island (most of the hexagonal islands seen in SEM or AFM do not show clear facets since their height is too small). Using x-ray diffraction to orient our samples, we find from the AFM measurements that the edges of the hexagonal structures (both facets and step bunches) have in-plane normal vectors of $\langle 1\bar{1}00\rangle$. This result is consistent with the previous report of $\{1\bar{1}01\}$ facet formation due to the presence of H.[4] Thus, it appears to be more energetically favorable for H to bond with $(1\bar{1}01)$ surfaces as compared with the (0001) surface.

Figure 2(a) shows an AFM image of a step-bunched sample grown in the presence of H (H_2 partial pressure of 2×10^{-6} Torr) that has undergone a postgrowth three-minute N_2+H_2 plasma exposure at 780 °C. We now observe small surface depressions on the flat terrace, as shown in Fig. 2(b). The lateral dimension of these depressions at the surface is about 0.1 μm and their depth varies from 2 to 6 nm. Studies of MOCVD-grown GaN films have found similar surface depressions and attribute them to the dislocations intersecting the surface.[1,9] For the sample here, it is likely that the surface depressions are filled with metallic Ga before annealing, as observed by Hsu *et al.*[12] Upon annealing in the presence of H, the Ga evaporates and steps surrounding the depression become H terminated, generating a MOCVD-like surface morphology. In summary, from the appearance of step bunching/facetting and surface depressions, the locations at which hydrogen preferentially bonds are found to be non-(0001) surface sites, such as step edges or facets around dislocation cores. On those sites, either there is less Ga coverage so that the H is able to bond, or the energetics prefer H termination over Ga.

Electrical studies have suggested that much of the leakage in GaN films occurs through dislocation cores.[12–14] We have used CAFM to evaluate the microscopic leakage properties of our films. In this technique, a conducting probe tip is brought into contact with a positively biased GaN film (unintentionally doped *n*-type), and the reverse bias leakage current is monitored while the tip scans over the surface. Figures 3(b) and 3(c) show the observed current for a GaN film grown *without* hydrogen, at reverse biases of 6 and 10 V. Figure 3(a) is the corresponding topography image. Conduction through isolated locations is clearly seen in Figs. 3(b) and 3(c). Figures 3(d)–3(f) show a similar set of images for a GaN film grown *with* the presence of hydrogen. These two films have similar screw dislocation densities and both are grown under Ga-rich conditions using HVPE GaN substrates. The H-treated sample does not show any leakage in the 10 pA range when a reverse voltage of 6 V is applied. At a reverse voltage of 10 V, this sample does show a few leakage spots, but with much lower density and less magnitude

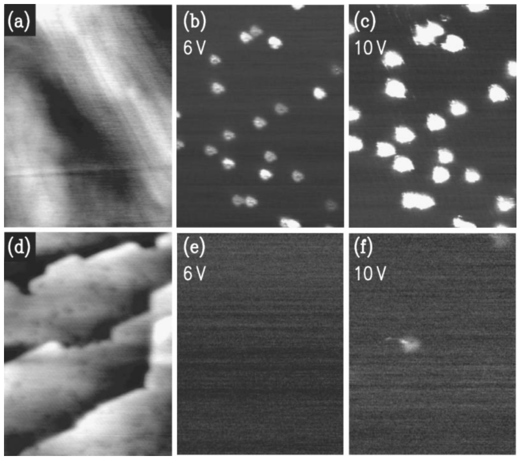

FIG. 3. (a) AFM topography of a GaN film grown without the presence of hydrogen, together with current images acquired at sample voltages of (b) 6 V and (c) 10 V. (d) AFM topography of a GaN film grown with the presence of hydrogen, together with current images acquired at (e) 6 V and (f) 10 V. All images have a size of $1.5\times2.0\ \mu m^2$. Gray scale ranges are 10 nm for (a) and (d), 20 pA for (b) and (c), and 10 pA for (e) and (f).

of leakage current compared with the non-H-treated film. Current–voltage measurements from macroscopic Schottky diodes were also made on GaN films grown with and without the presence of hydrogen. At 9 V reverse bias, the leakage current of the former is about $8\times10^{-3}\ A/cm^2$, which is 3 orders of magnitude less than that of the latter.

Our current–voltage measurements also reveal that the films grown *with* the presence of hydrogen show minimal leakage *independent* of whether postgrowth N_2+H_2 annealing has been performed. Thus, we associate the effect of H with a change in the structure of the dislocation cores (as opposed to a surface effect[15]). According to the results of Northrup,[8] H can modify the amount of Ga inside a dislocation core. Thus, we interpret our results as being due to this effect of H, thereby reducing the leakage through the dislocation cores. We conclude that the addition of a small amount of hydrogen during growth is beneficial in terms of the electrical properties of plasma-assisted MBE GaN films, although the concomitant surface facet formation may not be a desirable feature in the film growth.

In summary, we have studied the effect of introducing hydrogen gas through the rf-plasma source during PAMBE of Ga-polar GaN(0001). For small amounts of hydrogen, the Ga bilayer structure still prevails on the (0001) surface. Hydrogen is found to induce step bunching/facetting and surface depressions. The leakage current through dislocation cores is found to be reduced significantly due to the presence of hydrogen. It is deduced that H bonds most actively to sites such as step edges and locations around dislocation cores.

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