

Electronic structure of H/GaN(0001): An EELS study of Ga-H formation

V. J. Bellitto and B. D. Thoms*

Department of Physics and Astronomy, Georgia State University, Atlanta, Georgia 30303

D. D. Koleske, A. E. Wickenden, and R. L. Henry

Laboratory for Advanced Material Synthesis, Code 6861, Electronic Science and Technology Division, Naval Research Laboratory, Washington, D.C. 20375

(Received 8 March 1999)

Bare and hydrogenated GaN(0001) were characterized using electron-energy-loss spectroscopy (EELS), Auger electron spectroscopy (AES), and low-energy electron diffraction (LEED). AES and LEED show that the GaN surface is clean but faceted. EELS following hydrogen atom exposure shows a decrease in the intensity of the band-gap transition at 3.5 eV as well as the development of a previously unreported loss peak at 11.7 eV and quenching of a peak at 6.6 eV. We suggest that the peaks at 6.6 and 11.7 eV correspond to occupied states observed in photoemission lying near 1 and 6 eV below the valence-band maximum, respectively. These loss peaks indicate the participation of an unfilled electronic state ~ 2 eV above the conduction-band minimum. Hydrogen atom exposure also results in an increase in EELS intensity at 18 eV. Molecular hydrogen does not react with Ga-terminated GaN(0001). These changes in the electronic structure of GaN(0001) may be useful indicators of surface Ga-H. [S0163-1829(99)12831-5]

INTRODUCTION

Gallium nitride (GaN), along with its alloys with InN and AlN, are very promising materials for the production of high-temperature and high-power transistors as well as blue and uv emitters and detectors.¹⁻³ In this paper we report measurements of GaN surface electronic properties and the effect of hydrogen on those properties. Both adsorbates and surface preparation affect the surface electronic structure and therefore the band bending and potential barriers at interfaces.⁴⁻⁶ These potential barriers have a significant impact on the performance of high-power and high-frequency devices.⁶ In addition to electronic properties, hydrogen also affects processes necessary for device production. Hydrogen has been reported to affect growth rate and film quality for GaN produced by molecular-beam epitaxy (MBE) (Ref. 7) and metal-organic chemical vapor deposition (MOCVD),^{8,9} as well as doping efficiency¹⁰ and etch rates.¹¹ Recently, it has been reported that GaN can be etched by bombardment with low-energy electrons in a hydrogen atmosphere.¹²

Other researchers have shown that hydrogen adsorption affects the electronic structure of GaN(0001). Bermudez *et al.* observed a surface state by electron-energy-loss spectroscopy (EELS) and ultraviolet photoelectron spectroscopy (UPS) on the clean surface, which was removed by reaction with atomic hydrogen.¹³ Dhesi *et al.* performed angle-resolved photoemission spectroscopy and reported a surface state with sp_z character, consistent with a dangling-bond state, which was destroyed by the adsorption of activated H_2 .¹⁴

The authors have recently reported the results of a high-resolution electron-energy-loss spectroscopy (HREELS) study of hydrogen on GaN(0001).¹⁵ In that work it was reported that molecular hydrogen did not react with the GaN(0001) surface while atomic hydrogen exposure resulted in formation of surface Ga-H. No surface N-H was found

and it was concluded that the surface was Ga-terminated. In this work, we perform EELS to characterize the electronic structure of hydrogenated GaN(0001) and correlate the electronic structure with previous surface vibrational spectroscopy results.

EXPERIMENTAL DETAILS

This work was performed in a three-chamber stainless-steel ultrahigh-vacuum (UHV) system with a base pressure of 2×10^{-10} Torr. Details of the UHV system and sample mount have previously been described.¹⁵

The GaN sample used in this study was grown by MOCVD at the Naval Research Laboratory and is 5 mm wide \times 12 mm long.¹⁶ The GaN film was grown on *a*-plane sapphire, which was heated to 1180 °C for 10 min followed by the growth of a low temperature 250-Å-thick AlN layer at 600 °C. The AlN layer was ramped to the growth temperature under NH_3 to a temperature of 1040 °C for the growth of the GaN film. The GaN film was grown using TMGa and NH_3 with H_2 as a carrier gas. It is silicon doped with a carrier concentration of $2 \times 10^{17} \text{ cm}^{-3}$ and mobility of 400 $\text{cm}^2/\text{V s}$.

The sample was rinsed with acetone and then isopropyl alcohol before insertion into UHV. *In situ* sample cleaning was performed by a procedure of bombardment with $\sim 25 \mu\text{A}/\text{cm}^2$ of 1 keV nitrogen ions for 5 min and annealing in UHV at 900 °C for 5 min. This method of cleaning has been shown to leave a clean and well-ordered surface, although faceting has been reported.^{13,17,18} Cleanliness of the sample was verified by Auger electron spectroscopy (AES), which detected no oxygen or carbon to the instrument sensitivity of $\sim 5\%$ of a monolayer.

A dynamic backfill of H_2 was used for both molecular and atomic hydrogen dosing. Atomic hydrogen production was accomplished using a W filament heated to 1500 °C as pre-

viously described.¹⁵ Exposures using the heated W filament will be referred to as H* since the sample is simultaneously exposed to molecular and atomic hydrogen. Exposures are given in Langmuirs (L) of H₂, where 1 L = 1 × 10⁻⁶ Torr sec. The sample temperature during H* dosing remained at ~60 °C. Even after a large dose of 3000 L of H*, no carbon or oxygen was detected by AES.

EELS was performed using an incident electron energy of 90 eV, which has been reported to result in electron-stimulated desorption (ESD) of hydrogen from GaN.^{13,15} A more detailed study of hydrogen ESD from GaN(0001) will be published elsewhere.¹⁹ In order to minimize ESD effects, the incident current density was reduced as much as possible (~50 μA/cm²) while still yielding sufficient resolution (modulation amplitude = 0.25 V) and signal to noise. For all of the spectra shown, between four and twelve data sets have been normalized at a loss energy of 30 eV and averaged to achieve improved signal to noise. The scan time was minimized (~30 s) and each spectrum was acquired from a spot not previously irradiated. Scans begin at a loss energy of 30 eV and end at 2 eV. Although we have minimized the amount of hydrogen removed by ESD during acquisition of a spectrum, we have not eliminated it and none of the spectra presented should be taken as representative of a fully hydrogen-saturated surface. Auger electron spectra were acquired with a 3 keV incident electron beam and a modulation amplitude of 1.0 eV.

EELS data reported in the literature have often been acquired with a cylindrical mirror analyzer and lock-in amplifier which collects a signal proportional to $d(EN(E))/dE$. Although this does separate the loss-related features from the smooth background, the positions of peaks in $d(EN(E))/dE$ data do not correspond with energy states determined by other probes of electronic structure. Since peaks in inverted second derivative [$-d^2(EN(E))/dE^2$] spectra are expected to occur at the same energies as peaks in $N(E)$ and correspond more directly with other determinations of electronic structure, EELS data have sometimes been reported in this way. We have acquired EELS data using the retarding field method with a lock-in amplifier which yields $N(E)$. In addition to $N(E)$, we also report $d(EN(E))/dE$ and $-d^2(EN(E))/dE^2$ spectra for comparison to previously published work.

RESULTS AND DISCUSSION

After sputtering and annealing, a hexagonal 1 × 1 pattern with sharp spots and low background intensity was observed by low-energy electron diffraction (LEED) from GaN(0001) as previously reported.¹⁵ Although the LEED exhibited good contrast, faceting of the surface was quite evident.

Figure 1 shows the first-derivative EELS [$d(EN(E))/dE$] after sputtering and annealing, after 200 L of H₂ exposure, and after 200 L of H* exposure. We have verified using HREELS and AES that the sputtered and annealed GaN(0001)-(1 × 1) surface is free of hydrogen and other adsorbates. The EELS spectrum of the clean surface is similar to the spectrum reported by Bermudez *et al.*^{4,13,17} After molecular hydrogen exposure, EELS shows little difference from that of the clean surface. We interpret this as indicating that H₂ does not readily react with GaN(0001) near room

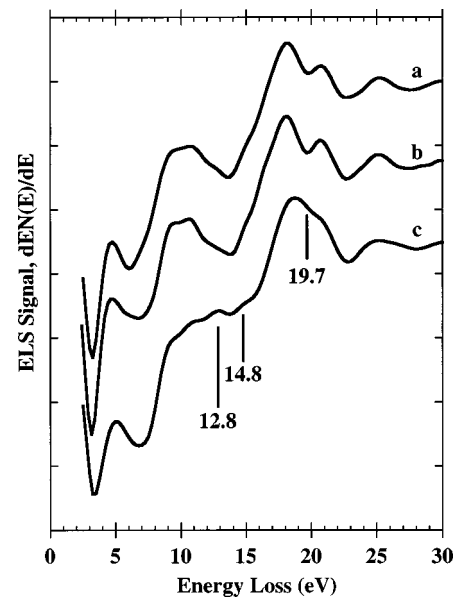


FIG. 1. First-derivative electron-energy-loss spectra of (a) sputtered and annealed GaN(0001) and following exposure to (b) 200 L of H₂ and (c) 200 L H*. During H₂ exposure the ion gauge was shut off after an initial pressure measurement. H* denotes molecular hydrogen in the presence of a hot W filament.

temperature. This conclusion is consistent with HREELS experiments performed on the same sample¹⁵ and also with results from other researchers.^{20,21} In contrast, significant changes are observed following H* exposure. In the first-derivative spectrum shown in Fig. 1, the double peak centered near 20 eV merges into a single peak with H adsorption. A leveling of the entire region from 9 to 15 eV is also seen, with reductions of the peak between 9 and 11 eV and the dip between 13 and 15 eV.

Figure 2 shows first-derivative EELS spectra following various H* exposures. These data show the beginnings of a

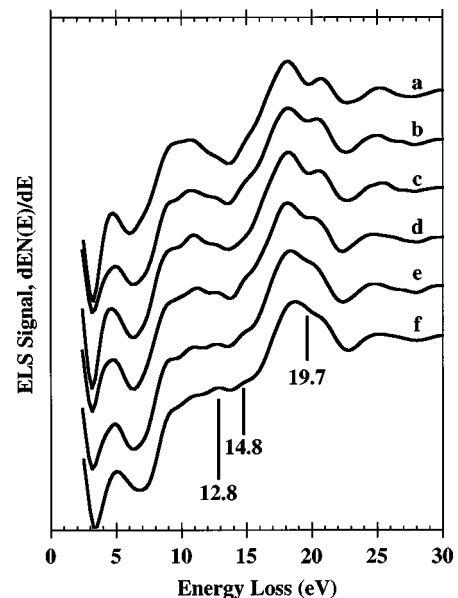


FIG. 2. First-derivative electron-energy-loss spectra of (a) clean GaN(0001) and following exposure to (b) 5 L, (c) 25 L, (d) 50 L, (e) 100 L, and (f) 200 L of H*.

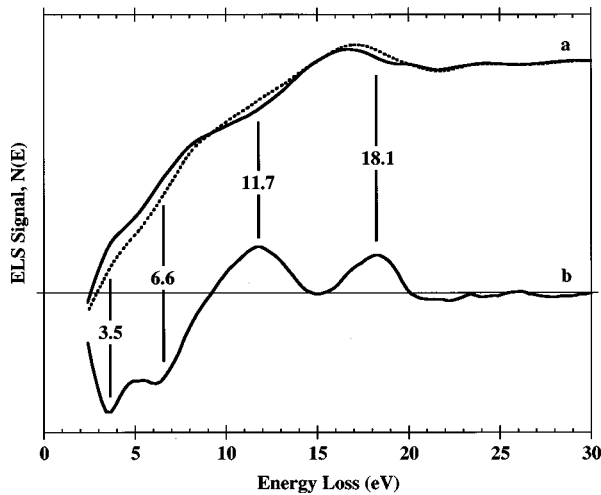


FIG. 3. Electron-energy-loss spectra of (a) clean GaN(0001) (solid line) and following 200 L of H^* exposure (dotted line) and (b) difference of spectra from hydrogenated and clean surfaces ($\times 5$).

flattening of the region from 9 to 15 eV and a merging of the double peak centered at 20 eV after exposures as small as 5 L. These changes progress continuously with increasing exposure and are nearly complete after 50 L. Spectra taken after 100 and 200 L H^* exposures appear identical, indicating that saturation occurs between 50 and 100 L of H^* exposure. These EELS results agree with previous HREELS results showing Ga-H vibrational features appearing after as little as 5 L and saturating near 50 L of H^* exposure.¹⁵

In order to understand the changes induced in the energy-loss spectrum by the adsorption of hydrogen, we next present both $N(E)$ and $-d^2(EN(E))/dE^2$ spectra of clean and hydrogenated GaN(0001). It must be noted that inverted second-derivative spectra emphasize changes in small but sharp features while minimizing broader changes easily observed in $N(E)$ data.

Figure 3(a) shows the $N(E)$ energy-loss spectra obtained from GaN(0001)-(1 \times 1) after sputtering and annealing and after 200 L of H^* exposure. Figure 3(b) shows the difference of hydrogenated and clean spectra. Hydrogenation produces large and broad intensity increases centered at 11.7 and 18.1 eV while somewhat sharper decreases occur at 3.5 and 6.6 eV. For comparison to previous EELS work on GaN, GaAs, GaP, and GaSb, we present in Fig. 4 the inverted second derivative of energy-loss spectra for clean and 200 L H^* exposed GaN(0001)-(1 \times 1). The inverted second-derivative spectrum of the clean surface reported here is very similar to previously published data.^{22,23}

Previous HREELS work on this same sample showed that exposure to atomic hydrogen produced only Ga-H with no evidence of surface N-H.¹⁵ In conjunction with HREELS, we attribute the changes observed in the energy-loss spectrum after exposure to H^* to the formation of a Ga-H surface species.

Both $N(E)$ and inverted second-derivative EELS show a peak at ~ 3.5 eV for the clean surface, which decreases in intensity upon hydrogenation. The peak at 3.5 eV has previously been assigned to the interband transition across the band gap.^{17,22,23} Bermudez *et al.* reported that even though a submonolayer coverage of O essentially eliminated this peak

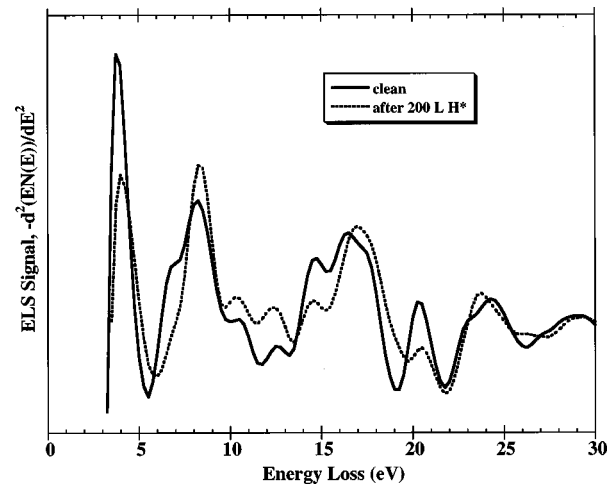


FIG. 4. Inverted second-derivative electron-energy-loss spectra of clean GaN(0001) (solid line) and following 200 L of H^* exposure (dotted line).

from the energy-loss spectrum, exposure to atomic hydrogen had no observable effect.¹³ They suggested that a high rate of ESD removed the hydrogen within the time required to obtain the spectrum. By minimizing the incident electron flux, we are able to observe a significant reduction in the intensity of the band-gap transition. However, since some hydrogen removal occurs during data acquisition, we do not know whether or not this peak is present on the fully saturated surface.

Both $N(E)$ and inverted second-derivative EELS also show a loss of intensity at ~ 6.6 eV upon atomic hydrogen exposure. Bermudez *et al.* have previously reported an H-induced change in single-derivative EELS near 7 eV,¹³ however the transition associated with the peak at 6.6 eV has not previously been assigned.

In Fig. 3, the $N(E)$ spectrum shows a broad increase in intensity at loss energies between 9 and 15 eV with the largest increase at 11.7 eV. This intensity increase is also responsible for the flattening occurring between 9 and 15 eV in first-derivative spectra shown in Figs. 1 and 2. Inverted second-derivative spectra in Fig. 4 also show an increase in intensity in this region. No previous assignments have been made for losses in this region from GaN.

Using photoemission, both Dhesi *et al.*¹⁴ and Bermudez *et al.*¹³ have reported that hydrogen adsorption produces a reduction in intensity near 1 eV below the valence-band maximum (VBM). This decrease in intensity has been assigned to the reaction of hydrogen with a surface state due to dangling bonds with sp_z character.¹⁴ Both groups have also reported a broad increase in intensity near 6 eV below the VBM upon H atom exposure.^{13,14} In this study, we observe a decrease in intensity in an energy-loss feature at 6.6 eV and a broad increase around 12 eV upon H atom exposure. We note that the separation between the EELS features is approximately the same as for the photoemission peaks (5 eV). Upon H adsorption, the lower-binding-energy photoemission peak and the lower-loss-energy EELS feature both decrease in intensity while the higher-binding-energy photoemission peak and the higher-loss-energy EELS feature both increase. We suggest that the EELS features at 6.6 and ~ 12 eV are associated with transitions from the occupied states observed

in photoemissions near 1 and 6 eV below the VBM. That would imply that they share a final state lying about 2 eV above the conduction-band minimum (CBM). Calculated band structures for GaN show a peak in the density of states lying about 2 eV above the CBM.^{24,25} A recent inverse photoemission study on GaN(0001) also shows an unoccupied band lying 2 eV above the conduction-band minimum at the Γ point.²⁶

The $N(E)$ EELS spectrum of the clean surface has a large peak near 16.5 eV and a small peak near 20 eV. As Fig. 3 shows, H^* exposure produces an increase in intensity at 18 eV along with the disappearance of the peak near 20 eV. Similar behavior is observed in the inverted second-derivative spectrum where the sharp peak at 20.3 eV is almost eliminated. The reduction in intensity of the peak at 20 eV results in the merging of the double peak centered at 20 eV in the first-derivative spectrum as seen in Fig. 1. Bermudez *et al.* reported similar changes upon reaction with hydrogen.¹³ The peak at 20 eV was previously assigned to coupled Ga 3*d*-to-conduction-band transitions and bulk plasmon excitations^{22,23} as well as overlapping volume plasmon and N 2*p* excitations.¹⁷ A loss peak at 20 eV has also been observed in EELS from the (110) surfaces of GaAs,^{22,23,27-31} GaP,³¹ and GaSb.³¹ Coverages of hydrogen,^{29,30} oxygen,^{27,29} and nitrogen^{22,23} on GaAs(110) have been shown to remove the 20 eV peak, which was attributed to an excitonic Ga 3*d* core-level-to-dangling-bond transition^{22,23,28-32} as well as a Ga intra-atomic transition.^{33,34} Since our HREELS study demonstrates that hydrogen reacts with surface Ga atoms to form Ga-H,¹⁵ we suggest that the peak at 20 eV is due to a Ga 3*d* core-level-to-dangling-bond transition. Although hydrogen adsorption nearly eliminates the 20 eV loss peak, oxygen adsorption on GaN(0001) has been reported to shift this peak 0.5 eV higher in loss energy.¹⁷

Next we discuss the increase in EELS intensity at 18 eV in $N(E)$. A volume plasmon has been predicted near 18.5 eV based on optical data,^{17,24} however the adsorption of hydrogen onto surface Ga sites would not be expected to significantly alter the volume plasmon loss intensity. A surface

plasmon is calculated from optical data to occur near 15 eV.^{17,24} A peak in the $-d^2(EN(E))/dE^2$ spectrum from clean GaN(0001) near 16 eV has previously been assigned to a surface plasmon.^{22,23} Examination of the $N(E)$ and inverted second-derivative spectra in this region suggests that the peak near 16 eV previously assigned to a surface plasmon may shift to higher loss energy upon hydrogen adsorption.

Since HREELS from this sample has shown that hydrogen bonds only on Ga sites and that GaN(0001) is Ga-terminated, we conclude that each of the changes observed here following H^* exposure is due to Ga-H formation. Therefore, titration with atomic hydrogen followed by EELS is a possible method for researchers to check the termination of GaN surfaces. Further work to identify signatures of N-H formation on GaN surfaces is still needed.

CONCLUSION

We have used surface-sensitive electron spectroscopy to examine the electronic structure of both clean and hydrogen-atom exposed GaN(0001). We have interpreted changes in the energy-loss spectrum in light of the result of HREELS work showing that after exposure to atomic hydrogen, surface Ga-H is present but N-H is not. Following adsorption of hydrogen onto Ga surface sites, we observe reductions in the EELS intensity for the band-gap transition at 3.5 eV and a Ga 3*d* core-level-to-dangling-bond transition at 20.3 eV. H adsorption is also seen to produce a broad intensity increase at 11.7 eV and a decrease at 6.6 eV. We suggest the loss peaks at 6.6 and 11.7 eV are associated with occupied states near 1 and 6 eV below the valence-band maximum and share a common final state at ~ 2 eV above the conduction-band minimum. A broad increase is also observed at ~ 18 eV.

ACKNOWLEDGMENTS

The authors wish to acknowledge Y. Yang for his assistance with these experiments and V. M. Bermudez for many helpful discussions. Work performed at the Naval Research Laboratory was supported by the Office of Naval Research.

*Author to whom correspondence should be addressed.

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