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Efficient electron-stimulated desorption of hydrogen from GaN(0001)

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Electron-stimulated desorption (ESD) of hydrogen from GaN(0001) has been observed and characterized using electron-energy-loss spectroscopy. Auger electron spectroscopy and low-energy electron diffraction show that the GaN surface is clean but faceted. As previously reported, saturation exposure to atomic hydrogen produces a decrease in the intensity of energy-loss peaks at 3.5 and 6.6 eV and an increase in the intensity of loss peaks at 11.7 and 18 eV. Bombardment with 90 eV electrons produces a reversal of the hydrogen-induced changes at 3.5, 6.6, and 11.7 eV. The increased intensity at 18 eV is almost unchanged by electron exposure. We conclude that the reversal of changes at 3.5, 6.6, and 11.7 eV is due to electron-stimulated desorption of hydrogen from Ga sites while the loss peak at 18 eV is due to bulk hydrogen and not affected by 90 eV electrons. Cross sections for removal of H and D are found to be $(2\pm1)\times10^{-17}$ and $(7\pm3)\times10^{-18}\,\mathrm{cm}^2$, respectively. The large cross section and small isotope effect for ESD of hydrogen from GaN indicates the participation of a long-lived excited electronic state. [S0163-1829(99)13931-6]

INTRODUCTION

Gallium nitride (GaN) and its alloys with InN and AlN have been studied because of their applications in red to uv light-emitting diodes, lasers, and detectors, as well as high-temperature, high-power, and high-frequency electronic devices.[1–3] To achieve high etch rates and anisotropy during etching of GaN, high temperatures,[3–5] reactive chemicals, and/or high ion energies are required.[3,6] The use of electron- or photon-stimulated processes for etching may be one method to avoid the use of reactive chemicals, damage produced by high ion energies, and material limitations imposed by high temperatures. Gillis *et al.* have recently reported that GaN can be etched by low-energy electron bombardment in a hydrogen atmosphere by a technique called low-energy electron-enhanced etching (LE4).[7] It is a low-damage dry-etching technique which uses 1–15 eV electrons and a reactive species (H) to achieve etch rates of 200 Å/min, avoids ion-beam damage, and gives anisotropic pattern transfer. The mechanism of LE4 etching in an H plasma remains to be explained. Electron-stimulated processing also has the advantage of being spatially selective, making possible the production of patterned surfaces without masking. Electron beam patterning of hydrogen-saturated Si surfaces has been achieved without masking using a scanning tunneling microscope (STM).[8–12]

Electron-stimulated surface processes have been studied for many years[13,14] and there are several models which have been proposed to account for electron-stimulated desorption (ESD). Menzel and Gomer[15] and Redhead[16] put forward a model (MGR model) which is a direct excitation process from an initial bonding state to an antibonding state that dissociates before it has time to relax. Knotek and Feibelman suggested an Auger process in which a nonradiative decay of the core hole takes place.[17] The core hole is filled by a valence electron and the excess energy ejects a second electron. The doubly ionized state experiences additional relaxation through the ejection of an atom or ion. A further mechanism suggested for ESD of H from Si at energies below the electron excitation threshold involves the multiple vibrational excitation of the Si-H bond.[18]

ESD of hydrogen from GaN(0001) has been previously reported by Bermudez *et al.*[19] They reported that 90 eV electrons with a current density of ~60 $\mu\mathrm{A/cm}^2$ efficiently removed hydrogen from the surface. The authors have recently reported the results of a high-resolution electron-energy-loss spectroscopy (HREELS) study of hydrogen on GaN(0001),[20] which concluded that hydrogen atoms adsorbed to Ga sites and that the surface is Ga-terminated. The authors also recently reported on the study of hydrogen on GaN(0001) using electron-energy-loss spectroscopy (EELS), which described changes in electronic structure observed in EELS after hydrogen adsorption on Ga sites.[21] In this work, we perform EELS, Auger electron spectroscopy (AES), and low-energy electron diffraction (LEED) to examine electron-stimulated desorption of hydrogen from GaN(0001). EELS is used to obtain the cross sections for electron-stimulated desorption of H and D from GaN(0001).

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.[20]

The GaN sample used in this study was grown by metal-organic chemical vapor deposition (MOCVD) at the Naval Research Laboratory and is $5\,\mathrm{mm}$ wide$\times12\,\mathrm{mm}$ long.[22] 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-

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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 $2 \times 10^{17}\,cm^{-3}$ and a mobility of 400 cm^2/V s.

The sample was cleaned with acetone and rinsed with isopropyl alcohol before insertion into UHV. *In situ* sample cleaning was performed by a procedure of bombardment with 1 keV nitrogen ions and annealing in UHV at 900 °C. This method of cleaning has been shown to leave a clean and well-ordered surface although faceting has been reported.[19–21,23] Cleanliness of the sample was verified by AES, which detected no oxygen or carbon to our sensitivity of ~5% of a monolayer.

A dynamic backfill of H_2 was used for atomic hydrogen dosing. Atomic hydrogen production was accomplished using a W filament heated to 1500 °C as previously described.[20] 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 H_2, where $1\,L = 1 \times 10^{-6}$ Torr sec. Previous experiments using HREELS (Ref. 20) and EELS (Ref. 21) have shown saturation of GaN(0001) to occur near 50 L H* using the same dosing procedure. 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.[19,21] In order to minimize the rate of ESD, the incident current density was reduced as much as possible ($I_B = 0.40\,\mu A$ and current density$=50\,\mu A/cm^2$) while still yielding sufficient resolution (modulation amplitude=0.25 V) and signal to noise. All spectra shown have been normalized at a loss energy of 30 eV. The scan time was minimized (≈34 s) and scans begin at a loss energy of 30 eV and end at 2 eV. Electron exposure was performed by the electron gun used for EELS during the acquisition of spectra, and successive spectra were acquired on the same sample spot. 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. In this work, EELS data are acquired using the retarding field method with a lock-in amplifier, which yields $N(E)$. For comparison to other published work of the clean GaN(0001) spectrum and because the first-derivative spectra emphasize the changes due to H adsorption, we also present $d(EN(E))/dE$ spectra. The first-derivative spectra are obtained by multiplying the $N(E)$ data by electron energy before differentiating numerically.

RESULTS AND DISCUSSION

After sputtering and annealing, a hexagonal 1×1 pattern with sharp spots and low background intensity was observed by LEED from GaN(0001) as previously reported.[20] Although the LEED exhibited good contrast, faceting of the surface was quite evident. We have verified using HREELS and AES that the sputtered and annealed GaN(0001)-(1×1) surface is free of hydrogen and other adsorbates. Figure 1 shows the first-derivative EELS $[d(EN(E))/dE]$ after sputtering and annealing, and after 200 L of H* exposure followed by various amounts of electron bombardment. For each spectrum, electron beam bombardment time and electron exposure at the beginning of each spectrum is given. The spectrum of the clean surface [Fig. 1(a)] is similar to previously reported clean GaN(0001)-(1×1) spectra.[19,21,23,24] There are considerable changes to the clean surface following 200 L H* exposure as seen in Fig. 1(b), which have previously been described.[21] The double peak centered near 20 eV merges into a single peak and a leveling of the entire region from 9 to 15 eV is also seen, with an elimination of the peak between 9 and 11 eV and the dip between 13 and 15 eV.

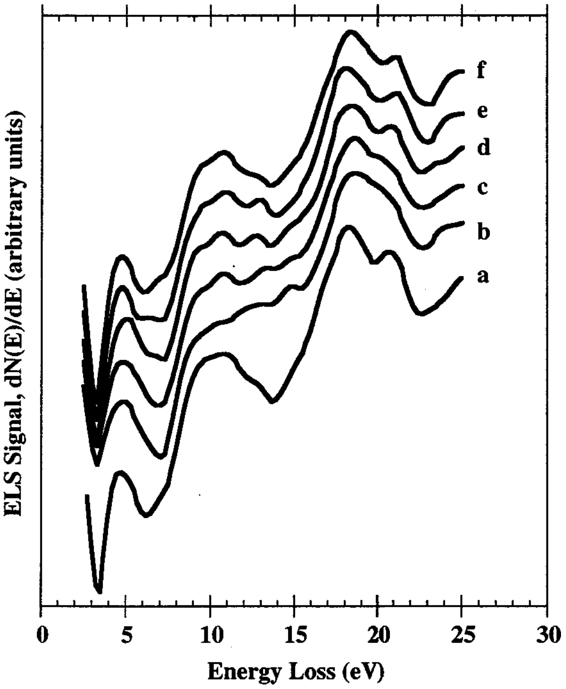

FIG. 1. First-derivative electron-energy-loss spectra $(dEN(E)/dE)$ of (a) sputtered and annealed GaN(0001) and successive spectra of the H-saturated GaN(0001) following electron exposures of (b) 0 electrons/cm^2 (0 min), (c) 1.9×10^{16} electrons/cm^2 (1 min), (d) 7.6×10^{16} electrons/cm^2 (4 min), (e) 1.5×10^{17} electrons/cm^2 (8 min), and (f) 3.8×10^{17} electrons/cm^2 (20 min). All spectra following hydrogenation were acquired from the same sample spot. In each case, the electron exposure and time given in parentheses correspond to the start of the spectrum.

With continued electron bombardment, substantial changes to the H-saturated surface are observed. What is apparent is that most of the change in the EELS spectrum occur within the first 8 min of electron bombardment. After 20 min, the EELS spectrum appears similar to the one acquired from the clean surface. The broad single peak of the 0-min spectrum centered near 20 eV emerges as a double peak following electron exposure. A reversal of leveling of the entire region from 9 to 15 eV is also seen, with a dip

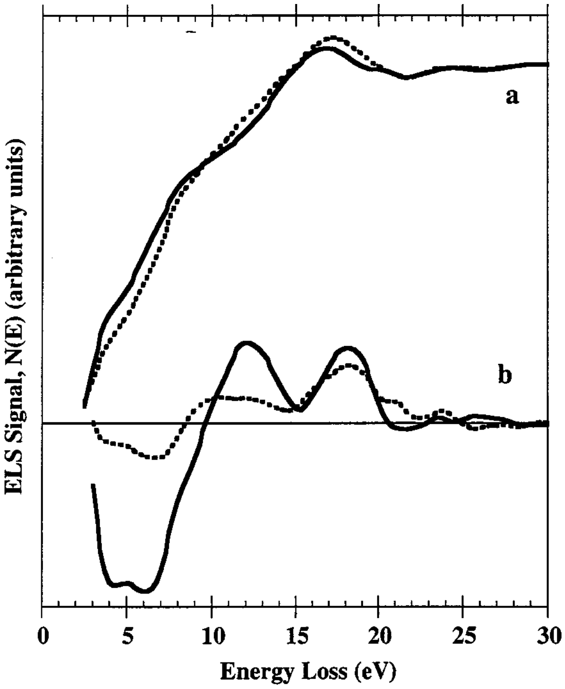

FIG. 2. (a) Solid line is electron-energy-loss spectrum $[N(E)]$ from clean GaN(0001) and the dotted line is the first spectrum following saturation hydrogen exposure (dotted line). (b) Solid line is the difference between $N(E)$ from the hydrogenated surface and $N(E)$ from the clean surface. Dotted line is the difference between $N(E)$ from the hydrogenated surface following 20 min of electron exposure and $N(E)$ from the clean surface.

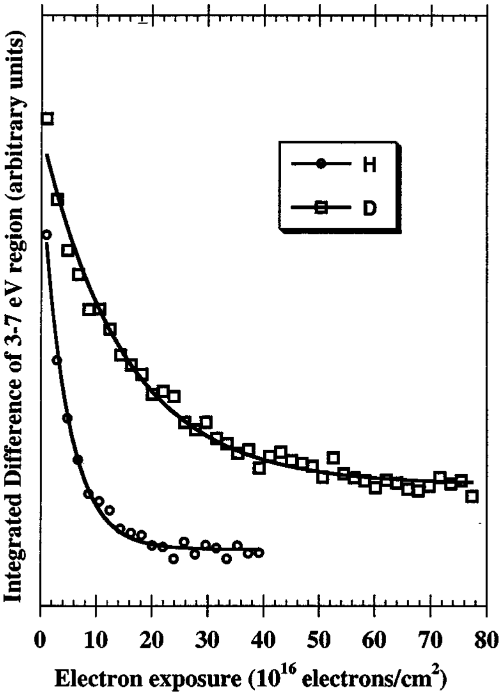

FIG. 3. Integral of the difference between $N(E)$ from the hydrogenated (deuterated) surface following various electron exposures and $N(E)$ from the clean surface vs electron exposure. Spectral region from 3 to 7 eV was integrated to calculate each point. The data are fitted to an exponential of the form $f(x)=A+Be^{-\sigma x}$, where σ is the desorption cross section (cm^2) and x is the electron exposure (electrons/cm^2).

reappearing between 13 and 15 eV.

In order to understand and quantify the changes induced in the energy-loss spectrum by electron exposure, we present $N(E)$ spectra of the clean and hydrogenated GaN(0001). Figure 2(a) shows the $N(E)$ energy-loss spectra for clean (solid line) and 200 L H* exposed (dotted line) GaN(0001). Figure 2(b) (solid line) is their difference, $N(E)$ from the hydrogen-saturated surface minus $N(E)$ from the clean surface. From this difference we see that H adsorption produces a decrease in the intensity at 3.5 and 6.6 eV and an increase in the intensity at 11.7 and 18.1 eV. The loss peak at 3.5 eV has been assigned to the band-gap transition. Loss peaks at 6.6 and 11.7 eV have been correlated to photoemission peaks affected by hydrogen exposure lying 1 and 6 eV below the valence-band maximum, respectively.[21] Since HREELS of H/GaN(0001) showed that only Ga-H species were produced by H exposure,[20] the hydrogen-induced changes in EELS are attributed to formation of Ga-H.[21]

Figure 2(b) (dashed line) shows the difference of $N(E)$ from the hydrogenated surface following 20 min of electron exposure and $N(E)$ from the clean surface. From this difference curve we see that electron exposure has substantially reversed the changes at 3.5, 6.6, and 11.7 eV produced by H exposure. We attribute the reversal of hydrogen-induced changes in EELS following electron exposure to ESD of hydrogen. Since electron exposure reverses changes produced by Ga-H formation, we suggest that electron-induced dissociation of the Ga-H bond is occurring. However, we cannot rule out the removal of surface Ga. The loss peak at 18 eV is much less affected by electron bombardment than peaks at 3.5, 6.6, and 11.7 eV. A volume plasmon has been predicted at 18.5 eV from optical data.[23] In earlier work we made no definitive assignment of this peak since formation of surface Ga-H would not be expected to affect the volume plasmon.[21] The lack of response of the 18 eV peak to electron exposures which substantially reverse other hydrogen-induced changes suggests that it is not associated with surface Ga-H but with subsurface or bulk hydrogen.

Similar to the curves shown in Fig. 2(b), we construct difference curves by subtracting the $N(E)$ energy-loss spectrum of the clean surface from the $N(E)$ spectra after various electron exposures of the hydrogen-saturated surface. To quantify the desorption process, we plot the integral of the difference from 3 to 7 eV versus the electron exposure as shown in Fig. 3. The points are fit to an exponential of the type $f(x)=A+Be^{-\sigma x}$, where σ is the desorption cross section (cm^2) and x is electron exposure (electrons/cm^2). The cross section for the ESD of H determined by this fit is $(2\pm1)\times10^{-17}\,\mathrm{cm}^2$, while the ESD of deuterium shows a cross section of $(7\pm3)\times10^{-18}\,\mathrm{cm}^2$, a factor of 3 lower than for H.

The 3–7-eV region was chosen for a larger region of integration, i.e., more signal, however the cross section for desorption of H can be determined for individual spectral features. Cross sections for the 3–4, 6–7, and 11–12 eV regions were found to be $(3\pm1)\times10^{-17}\,\mathrm{cm}^2$, $(2\pm1)\times10^{-17}\,\mathrm{cm}^2$, and $(1\pm0.5)\times10^{-17}\,\mathrm{cm}^2$, respectively. Different spectral regions produce cross sections within a factor of ~2 of each other. Since our previous HREELS work showed that there is only one surface adsorption site, we suggest that

TABLE I. Comparison of desorption cross sections from semiconductors.

Adsorbate	Substrate	Beam energy (eV)	Cross section (cm^2)	Reference
H/D	GaN(0001)	90	$2\times10^{-17}/7\times10^{-18}$	This work
H/D	Si(100)	7–12	$4\times10^{-21}/8\times10^{-23}$	18 and 26
H	Si(100)	8–30	3×10^{-20}	27
H	Si(100)	25–200	$(1\times10^{-19})-(1.4\times10^{-18})$	28
D	Si(111)	16–500	$<(1\times10^{-21})-(1.3\times10^{-20})$	29

the differences in our determination of cross sections are due to differences in the dependence of EELS features at 3.5, 6.6, and 11.7 eV on H coverage.

ESD of H from the GaN surface is a highly efficient process. Describing the ESD rate in terms of a quantum efficiency may better illustrate this. Assuming one Ga atom per unit cell and one H atom per surface Ga for the hydrogen-saturated surface, one can deduce an efficiency for the ESD process of $\sim$30 ($\sim$100) electrons for each H (D) atom desorbed. A cross section for the ESD of absorbed H from Ga–group-V semiconductor surfaces has not been reported in the literature, although ESD of hydrogen from GaAs(100) has been observed.[25] Table I compares the cross section determined here to previously reported cross sections for ESD of hydrogen from Si surfaces. The cross section for the ESD of hydrogen from GaN(0001) is two to four orders of magnitude greater than reported on Si surfaces. On GaN, the cross section for ESD of D is approximately three times smaller than for H, while on Si(100) the ESD of D is $\sim$50 times slower than for H.[26] Assuming the ESD of H from GaN(0001) occurs through an electronically excited state, as in the MGR model, the presence of a large cross section and small isotope effect would indicate slow quenching of the excited electronic state. In general, long-lived surface electronic excitations would result in enhanced efficiencies for electron- or photon-stimulated processes. Gillis *et al.* have reported that the LE4 process can etch both GaAs and GaN in pure hydrogen and infer the ‘‘existence of a low-energy electron-enhanced reaction channel not available to Ga and H in ordinary thermal reactions.’’[7] A longer-lived excited state associated with a surface Ga-H species as suggested by the present work may provide this reaction channel.

This extremely fast ESD of H has consequences for electron spectroscopies, such as LEED and EELS, which are performed in this range of electron energies and current densities.[19] For example, under the conditions used in these experiments (90 eV, 50 μA/cm^2), 34% of the surface H is removed in the first minute of electron exposure. In essence, the H is removed from GaN(0001) more quickly than many electron spectroscopies are usually performed.

CONCLUSION

We have used surface-sensitive electron spectroscopies to examine and quantify electron beam effects on the hydrogen-atom exposed GaN(0001) surface. Atomic hydrogen exposure produces changes in the energy-loss spectrum, decreases in intensity at 3.5 and 6.6 eV and increases in intensity at 11.7 and 18 eV. Electron bombardment of the hydrogen-saturated surface substantially reverses the changes at 3.5, 6.6, and 11.7 eV, restoring an energy-loss spectrum similar to that of the clean surface. We conclude that electron-stimulated desorption of hydrogen from surface Ga-H is responsible for these reversals. The increased intensity at 18 eV is not reversed by electron bombardment. We conclude that this feature is due to a volume plasmon and that hydrogen is being introduced into the subsurface or bulk. A very large cross section for ESD of H of $(2\pm1)\times10^{-17}\,cm^2$ was found with a reduction of $\sim$3 for the ESD of D to $(7\pm3)\times10^{-18}\,cm^2$. These results suggest the participation of a long-lived surface electronic excitation leading to desorption.

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