Eur. Phys. J. B **16**, 3–6 (2000)

THE EUROPEAN PHYSICAL JOURNAL B

EDP Sciences

Rapid Note

HREELS investigation of hydrogenated and deuterated GaN{0001} surfaces

S.P. Grabowski[a], H. Nienhaus, and W. Mönch

Laboratorium für Festkörperphysik, Gerhard-Mercator-Universität Duisburg, 47048 Duisburg, Germany

Received 1 February 2000

Abstract. The vibrational properties of clean, H- and D-covered GaN{0001} surfaces were investigated by high-resolution electron energy-loss spectroscopy. Auger electron spectroscopy and low-energy electron diffraction were utilized to monitor the surface cleanliness and structure, respectively. At the clean surface the Fuchs-Kliewer surface phonon frequency was determined to 700 cm^{-1} (86.8 meV). For the adsorbate-covered surfaces current structure models predict only Ga-H vibrations for surfaces of either polarity. Despite of this, the HREEL-spectra of the hydrogenated sample show a new loss structure at 3255 cm^{-1} (403.6 meV) and a shoulder at 1900 cm^{-1} (235.6 meV) which are attributed to N-H and Ga-H stretching vibrations, respectively. After deuterium exposure an isotope shift occurs. Again, a N-adsorbate vibration is clearly resolved. A Ga-D bending mode is observed at 390 cm^{-1} (48.4 meV), indicating that vibrations of both species are present.

PACS. 82.65.My Chemisorption – 68.35.Ja Surface and interface dynamics and vibrations – 79.20.-m Impact phenomena (including electron spectra and sputtering)

1 Introduction

The impetus to fabricate short-wavelength opto-electronic as well as high-temperature-resistant devices has focused much attention towards GaN lately. However, there are still many open questions concerning surface properties and adsorption behavior. Knowledge about these issues is essential to gain a better understanding of device properties and growth issues.

Because of its simplicity, hydrogen is a suitable candidate for any adsorption experiment in this context, but the results have been contradictory so far. One group [1] interprets their data such that hydrogen binds to Ga only, while another one [2] concludes a binding to both species. According to theoretical predictions, solely H-Ga bonds are to be expected, since regardless of surface polarity, the outermost layer of reconstructed surfaces always consists of Ga [3].

In this paper we attempt to clarify this issue by presenting results from high-resolution electron energy-loss spectroscopy (HREELS) investigations of hydrogenated and deuterated GaN{0001}. HREELS is a suitable tool for such an investigation, since it allows direct detection of hydrogen. Another advantage is that any electron-stimulated desorption of H which was found to occur at primary electron energies E_p exceeding 90 eV [4,5] should be negligible in the E_p regime used here.

2 Experimental

As sample material we used hexagonal GaN{0001} epilayers on Al_2O_3, grown by metal-organic vapor-phase epitaxy (MOVPE), which are commercially available from Cree Research, Inc. The surface polarity has not been specified by the vendor. Therefore, we use the nomenclature {0001} instead of (0001) or $(000\bar{1})$ to emphasize that the direction of the *c*-axis is unknown. The samples are nominally undoped, their electron density was specified to $n < 5 \times 10^{16}$ cm^{-3}.

The samples were cleaned by a two step procedure. At first they were etched in 50% hydrofluoric acid (HF) for 2 min, followed by a dip in de-ionised water. After removal from the liquid the specimen was blown dry with N_2 gas and immediately inserted into the vacuum system. The *in-situ* procedure consists of the deposition of 200 Å Ga and its removal by annealing at 800-850 °C. Surface cleanliness was checked by electron-excited Auger electron spectroscopy (AES) with a primary electron energy of 3 keV. No surface contaminants other than traces of carbon were found. Low-energy electron diffraction (LEED) images show 1×1 patterns which exhibit a multiplet structure

[a] e-mail: sgrabowski@uni-duisburg.de

consisting of an array of six circular-arranged spots [6,7] which is an indication for the presence of surface steps [7].

H_2 and D_2 molecules were thermally dissociated at a hot tungsten filament (2300 K). During exposure the pressure was monitored with a cold cathode gauge (IKR) only to avoid any undesired stimulation of H_2/D_2 molecules. Exposures are given in Langmuirs (1 L = 10^{-6} torr s) of H_2 and D_2 and were varied between 10 and 3×10^4 L.

The HREEL spectra were recorded in specular scattering geometry using an ELS90 [8] spectrometer. The energy of the incoming electrons E_p was adjusted to 12 eV and the angle of incidence to 60°. The instrumental resolution was deliberately set to 56 cm^{-1} (6.9 meV) to obtain higher count rates.

3 Results and discussion

Figure 1a displays a HREEL spectrum for a hydrogenated surface. The prominent loss structures labeled FK1 to FK4 as well as ν_{Ga-C} at the low-energy end of FK1 are present at clean surfaces also [9]. The former are due to single and multiple excitations of Fuchs-Kliewer-(FK) surface phonons [10]. Their single excitation energy amounts to 700 cm^{-1} (86.8 meV) which value is in good agreement with results from other studies [1,2,9,11,12]. The loss feature ν_{Ga-C} is found at 583 cm^{-1} (72.3 meV). It has been interpreted as Ga-C stretching vibration due to residual C atoms [9].

After hydrogenation H-induced features at 1900 cm^{-1} (235.6 meV) and 3255 cm^{-1} (403.6 meV), whose respective combination losses with a FK-phonon are labeled ν', as well as impurity-induced structures arise. The latter can be identified as N-OH stretching vibrations ν_{N-OH} [13] at 855 cm^{-1} (106.0 meV) and O-H stretching vibrations ν_{O-H} [14] at 3650 cm^{-1} (452.6 meV). Another contamination-related peak, δ_{O-H} at 1645 cm^{-1} (204.0 meV) originates either from a O-H bending mode [14] or a combination loss of ν_{N-OH} with a FK phonon. All these impurity-induced structures are due to dissociative adsorption of residual water molecules.

The H-induced loss structure at 1900 cm^{-1} is assigned to a H-Ga stretching vibration ν_{H-Ga}. Its loss energy is a little larger than what is found at hydrogenated GaAs(110)-surfaces [15–18] but is in good agreement with values from other groups [1,2]. The interpretation for the other hydrogen-induced peak varies. Sloboshanin *et al.* [2] assign it to a H-N stretching vibration ν_{H-N}, whereas Belitto *et al.* [1] rule out the existence of such a vibration. They explain this peak by a combination loss of ν_{H-Ga} with two FK-phonons. Taking the respective loss energies into account, one would expect the structure in question at 1900 cm^{-1} + 2 × 700 cm^{-1} = 3300 cm^{-1}, indeed in the range of the observed structure.

The comparison with a deuterated surface should clarify this issue. After D exposure one expects an isotope shift towards smaller frequencies. In the harmonic approximation the energy $\hbar\omega$ of a two-center vibration is proportional to the reciprocal square root of the reduced mass (*e.g.* Ref. [19]). If one assumes that H or D atoms move against the whole semiconductor crystal, *i.e.*, the reduced mass is set to equal the mass of hydrogen or deuterium, respectively, the excitation energy ratio $\hbar\omega_H/\hbar\omega_D$ is expected to be $\sqrt{2}$. Hence, one should look for the D-N vibration at a loss energy a little larger than 2300 cm^{-1}. In case the structure ν_{H-N} originates from a combination loss of ν_{H-Ga} with two FK-phonons, it should shift after deuteration towards a value of 1345 cm^{-1}+2×700 cm^{-1} = 2745 cm^{-1}, since the frequency of the FK-phonon is uneffected by the presence of adsorbates [18]. The latter is close to FK4 and is most likely to be obscured by its strong intensity. Belitto *et al.* [1] did not detect any of these D-induced structures in their HREEL-spectra due to a high full width at half maximum of 160 cm^{-1}. They concluded the existence of D-Ga bonds only.

To elucidate this issue, we conducted our HREELS experiments with a higher resolution resulting in peak-width of 80 cm^{-1}. Then, a D-N stretching vibration ν_{D-N} at 2395 cm^{-1} (297.0 meV) and even a combination

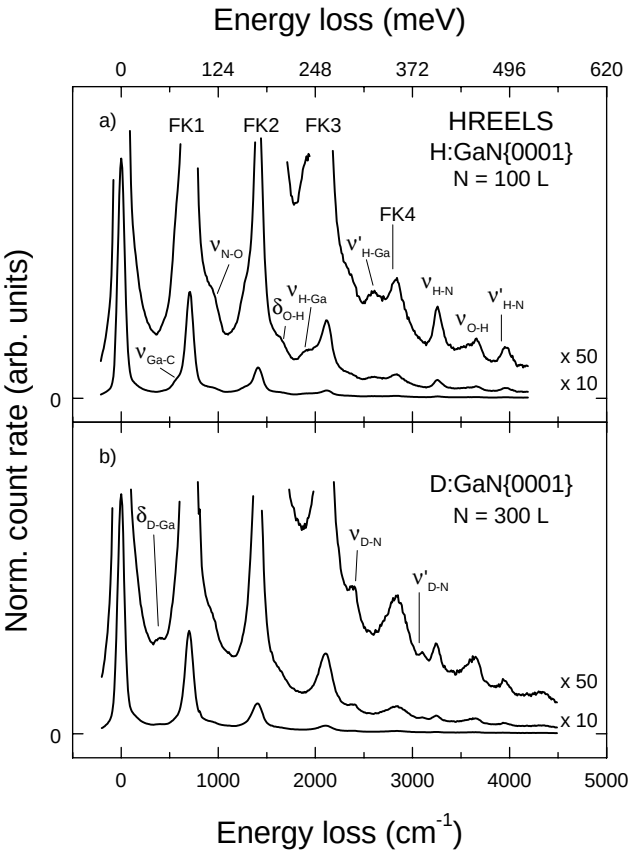

Fig. 1. High-resolution electron energy-loss spectra recorded with (a) H- and (b) D-covered GaN{0001} surfaces. The count rate of the quasi-elastic peak was normalized to 1. Loss structures FK1 to FK4 are due to single and multiple excitations of Fuchs-Kliewer phonons. The labels ν and δ assign stretching and bending vibrations of the respective molecular groups. The spectra were recorded in specular geometry with an angle of incidence of $\vartheta = 60°$. The primary electron energy E_p amounts to 12 eV. The instrumental resolution was set to 56 cm^{-1} (6.9 meV).

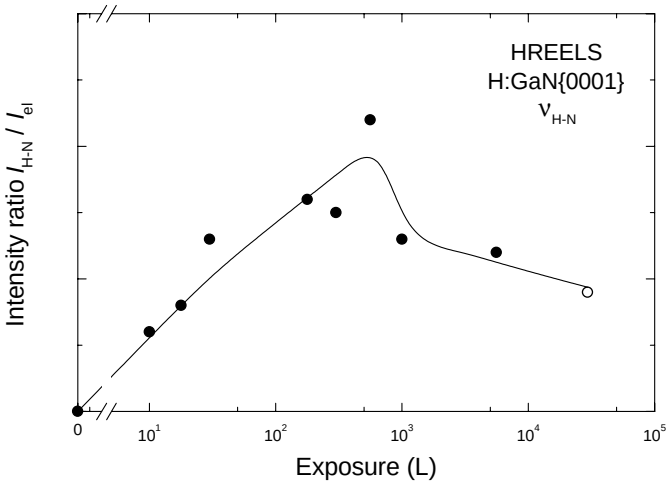

Fig. 2. Intensity ratio of the H-N stretching vibration and the quasi-elastic peak as a function of hydrogen exposure. The 3×10^4 L exposure (o) was conducted with an increased filament sample distance. The solid line is meant to guide the eye.

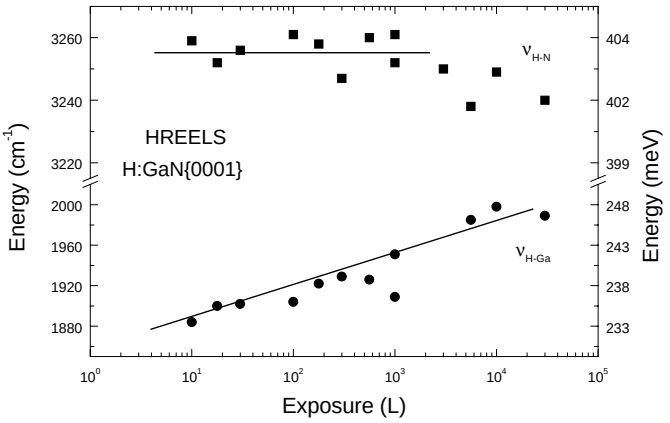

Fig. 3. Loss energy of the H-N and H-Ga stretching vibrations as a function of hydrogen exposure.

loss with a FK-phonon $\nu'_{\mathrm{D-N}}$ are clearly resolved after deuteration (Fig. 1b). Its vibrational energy is somewhat larger than anticipated, but this effect is owing to the anharmonicity of the bond potential and has been observed for other semiconductors as well [15,20]. Since D-N vibrations are present on the GaN{0001} surface, the $\nu_{\mathrm{H-N}}$ structure in Figure 1 can certainly be attributed to a H-N stretching mode. Theory [3] predicts the existence of H-Ga vibrations only. This discrepancy is due to different surface morphologies. There, ideal reconstructed surfaces were theoretically investigated, here we have to deal with stepped surfaces. The respective $\nu_{\mathrm{D-Ga}}$ valence vibration is to be expected at 1345 cm^{-1}. It is not visible in the spectra, because it is superimposed by FK2. A further D-induced structure is found at 390 cm^{-1} (48.4 meV) and is assigned to a D-Ga bending vibration $\delta_{\mathrm{D-Ga}}$. A comparison with GaAs(110) reveals the presence of such bending modes after H and D exposure at $\delta_{\mathrm{H}} = 515$ cm^{-1} and $\delta_{\mathrm{D}} = 387$ cm^{-1}, respectively [16]. The detection of the respective gallium bending mode at the hydrogenated surface is inhibited by the presence of $\nu_{\mathrm{Ga-C}}$.

At the deuterated sample $\nu_{\mathrm{H-N}}$ is still visible, although reduced in intensity, whereas $\nu_{\mathrm{H-Ga}}$ cannot be resolved from the background anymore. This H-induced loss feature most likely originates from residual water molecules since OH-vibrations were always detected in any spectrum and it has been shown that GaN{0001} is very receptive of H_2O [2].

Of further interest is the evolution of the hydrogen-uptake. Figure 2 depicts the intensity ratio of $\nu_{\mathrm{H-N}}$ and the quasi-elastic peak as a function of hydrogen exposure. The solid line is meant to guide the eye. One can observe an increase in intensity with increasing exposure until about 500 L. Then, the intensity drops off over a small exposure range, followed by a further but less rapid decrease at highest dosages. The determination of the loss intensity for $\nu_{\mathrm{H-Ga}}$ is more difficult since it is superimposed by $\nu''_{\mathrm{Ga-C}}$. Qualitatively, a similar behavior is found, though.

A decrease in HREELS intensity with increasing exposure may be explained by either a change in the H-substrate excitation probability or the onset of etching. The former may be caused by structural changes, *i.e.*, disrupture of the surface. In case etching occurs, a removal of surface atoms takes place by forming volatile molecules like NH_3, N_2 or GaH_3, for instance. These would desorb and thereby cause a reduction of hydrogen at the surface. The earliest stage of such processes would be an adsorbate-induced breaking of Ga-N bonds. This will lead to the formation of dihydrides. This can only happen, when an excess of hydrogen is available, that is, the number of hydrogen atoms impinging on the surface must exceed the number of empty adsorption sites.

We believe etching according to the above process description takes place at high exposures and, therefore, interpret the H-uptake diagram as follows: In the low-exposure regime, H atoms from the gas phase saturate surface dangling bonds. At higher dosages the probability for impinging H to encounter a H-substrate configuration and react with it to form dihydride-species increases. This causes a further increase in the hydrogen-uptake. Upon further hydrogenation, H desorbs from the surface by forming volatile molecules. The existence of such dihydride modes has been shown for GaAs(110) [16,17] and InP(110) [20]. From molecular data one finds characteristic dihydride scissor vibrations at 750 cm^{-1} (93.0 meV) for H_2-Ga and 530 cm^{-1} (65.7 meV) for D_2-Ga [21]. The respective scissor mode for H_2-N is to be expected at about 1550 cm^{-1} (192.2 meV) [22,23]. None of them are detected here, maybe because some of the mentioned vibrations are obscured by the large intensity of FK or multiple excitations thereof. Ultimately, no decision can be made if and how any etching occurs.

Another hint on the adsorption behaviour can be obtained from analysing the vibrational frequencies as a function of H-exposure. In Figure 3 this is shown for $\nu_{\mathrm{H-Ga}}$ and $\nu_{\mathrm{H-N}}$. The excitation energy for $\nu_{\mathrm{H-Ga}}$ has been obtained by determining the center frequency of a Voigt-type

profile fit. A linear shift from 1884 to 1990 cm^{-1} (233.6 to 246.8 meV) is observed whereas the vibrational energy of ν_{H-N} remains constant over an extended exposure range and only indicates a slight decrease at highest dosages.

An energy shift towards larger excitation energies can be explained by dipole- dipole interaction. Such shifts were reported earlier at Cl- [24], F- [25], and H-covered GaAs(110) surfaces [16,17]. However, the magnitude of the shifts observed here is rather unlikely for mere dipole-dipole interaction. Therefore another explanation is favored, namely the appearance of new vibrational states at higher energies which cannot be resolved as a separate component. Such a high-energy component has been reported for H:GaAs(110) [17] and was assigned to the onset of surface etching.

4 Conclusions

In conclusion, hydrogen binds to both gallium and nitrogen on stepped GaN{0001} surfaces. This result was deduced from the detection of both H-Ga and H-N stretching vibrations at 1900 cm^{-1} (235.6 meV) and 3255 cm^{-1} (403.6 meV), respectively. The existence of the latter was confirmed by the presence of a D-N stretching mode at 2395 cm^{-1} (297.0 meV) after deuteration. Furthermore, a D-Ga bending vibration was found at 390 cm^{-1} (48.4 meV).The hydrogen-uptake increases with increasing exposure in the low coverage regime. Then, at exposure exceeding 500 L a decrease in the intensity of the H-N stretching vibration is found. This might be explained by surface etching. A frequency shift towards larger excitation energies has been found for the H-Ga stretching vibration. This may be explained by the appearance of a high-frequency component which cannot be resolved separately.

This work was partially supported by the Deutsche Forschungsgemeinschaft under contract number Mo 318/28-2.

References

1. V.J. Belitto, B.D. Thoms, D.D. Koleske, A.E. Wickenden, R.L. Henry, Surf. Sci. **430**, 80 (1999).
2. S. Sloboshanin, F.S. Tautz, V.M. Polyakov, U. Starke, A.S. Usikov, B.Ja. Ber, J.A. Schaefer, Surf. Sci. **427/428**, 250 (1999); F.S. Tautz, S. Sloboshanin, U. Starke, J.A. Schaefer, J. Phys. Cond. Matter **11**, 8035 (1999).
3. A.R. Smith, R.M. Feenstra, D.W. Greve, J. Neugebauer, J.E. Northrup, Phys. Rev. Lett. **79**, 3934 (1997).
4. V.M. Bermudez, D.D. Koleske, A.E. Wickenden, Appl. Surf. Sci. **126**, 69 (1998).
5. V.J. Bellitto, B.D. Thoms, D.D. Koleske, A.E. Wickenden, R.L Henry, Phys. Rev. B **60**, 4821 (1999).
6. V.M. Bermudez, T.M. Jung, K. Doverspike, A.E. Wickenden, J. Appl. Phys. **79**, 110 (1996).
7. O. Janzen, Ch. Hahn, T.U. Kampen, W. Mönch, Eur. Phys. J. B **7**, 1 (1999).
8. H. Ibach, M. Balden, D. Bruchmann, S. Lehwald, Surf. Sci. **269/270**, 94 (1992).
9. S.P. Grabowski, T.U. Kampen, H. Nienhaus, W. Mönch, Appl. Surf. Sci. **123/124**, 33 (1998).
10. R. Fuchs, K.L. Kliewer, Phys. Rev. **140**, A2076 (1965).
11. Z.Q. He, X.M. Ding, X.Y. Hou, X. Wang, Appl. Phys. Lett. **64**, 315 (1994).
12. P. Gassmann, G. Schmitz, R. Franchy, Surf. Sci. **380**, L459 (1997).
13. R.T. Hall, G.C. Pimentel, J. Chem. Phys. **38**, 1889 (1963).
14. G. Herzberg, *Molecular Spectra and Molecular Structure, Vol. II, Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand Reinhold, New York, 1945).
15. H. Lüth, R. Matz, Phys. Rev. Lett. **46**, 1652 (1981).
16. S.P. Grabowski, H. Nienhaus, W. Mönch, Surf. Sci. **352-354**, 310 (1996).
17. H. Nienhaus, S.P. Grabowski, W. Mönch, Phys. Stat. Sol. A **159**, 175 (1997).
18. L.H. Dubois, G.P. Schwartz, Phys. Rev. B **26**, 794 (1982).
19. H. Goldstein, *Classical Mechanics* (Addison-Wesley, Reading, 1991).
20. H. Nienhaus, S.P. Grabowski, W. Mönch, Surf. Sci. **368**, 196 (1996).
21. N.N. Greenwood, A. Storr, M.G.H. Wallbridge, Inorg. Chem. **2**, 1036 (1963).
22. P.T. Cunningham, V.A. Maroni, J. Chem. Phys. **57**, 1415 (1972).
23. K.O. Christe, Inorg. Chem. **14**, 2821 (1975).
24. J. Pankratz, H. Nienhaus, W. Mönch, Surf. Sci. **307-309**, 211 (1994).
25. H. Nienhaus, W. Mönch, Appl. Surf. Sci. **104/105**, 95 (1996).