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Carbon impurities and the yellow luminescence in GaN
Infrared absorption of hydrogen-related defects in ammonothermal GaN

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Polarization controlled Fourier transform infrared (FTIR) absorption measurements were performed on a high quality m-plane ammonothermal GaN crystal grown using basic chemistry. The polarization dependence of characteristic absorption peaks of hydrogen-related defects at 3000–3500 cm⁻¹ was used to identify and determine the bond orientation of hydrogenated defect complexes in the GaN lattice. Majority of hydrogen was found to be bonded in gallium vacancy complexes decorated with one to three hydrogen atoms (V_{Ga}H_{1,2,3}) but also hydrogenated oxygen defect complexes, hydrogen in bond-center sites, and lattice direction independent absorption were observed. Absorption peak intensity was used to determine a total hydrogenated V_{Ga} density of approximately 4 × 10¹⁸ cm⁻³, with main contribution from V_{Ga}H_{1,2}. Also, a significant concentration of electrically passive V_{Ga}H₃ was detected. The high density of hydrogenated defects is expected to have a strong effect on the structural, optical, and electrical properties of ammonothermal GaN crystals. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4952388]

Gallium nitride (GaN) is used for numerous commercial devices such as blue-green light emitters and high power transistors. Current GaN technology relies on heteroepitaxial growth leading to dislocations, mosaic crystal structure, stress, and wafer bowing, all detrimental to device performance. To circumvent these problems, native GaN substrates are needed for next generation light emitters and power transistors.1 The ammonothermal method is regarded as one of the most feasible methods to grow high quality bulk GaN crystals, due to its scalability and high efficiency.2–4

GaN crystals grown by the basic ammonothermal method contain a significant concentration of gallium vacancy-related defects (10¹⁸ cm⁻³) and hydrogen (10¹⁹ cm⁻³).5,6 Gallium-vacancies (V_{Ga}) and their complexes can be detected by positron annihilation spectroscopy7 and optical absorption measurements,6,8 and their properties have been simulated by first principles calculations.9,10 Hydrogenated gallium vacancy complexes (V_{Ga}H) form deep levels in the band-gap,6,10,11 add scattering centers limiting the carrier mobility, and contribute to sub-bandgap optical absorption,12 and have been associated with device degradation.11,13 The formation energies of V_{Ga} complexes are calculated to be lower than that of isolated V_{Ga}.10 Thus, the majority of V_{Ga} in as-grown ammonothermal material is complexed with hydrogen which is present in large amounts in the ammonothermal growth atmosphere.14 In addition to vacancy complexes, hydrogen can exist in anti-bond (AB), bond-center (BC), and interstitial sites in the GaN lattice.15 Also, other impurities such as carbon and oxygen are known to form complexes with V_{Ga}.16,17

N-H bonds in a semiconductor lattice have vibrational stretch frequencies in the mid-infrared range, and their absorption can be detected using Fourier transform infrared (FTIR) spectroscopy. FTIR has been used to detect V_{Ga}H complexes in GaN crystals grown by the ammonothermal method6,8 and in proton irradiated GaN films.15,18 However, due to the scarcity of high quality bulk GaN samples, no detailed reports on the infrared absorption of V_{Ga}H complexes exists. FTIR has been extensively used in characterization of hydrogen complexed defects in other semiconductors materials, e.g., ZnO,19 SnO,20 and dilute III-N-V alloys.21

In this letter, we report on the detection and analysis of hydrogenated defects in ammonothermal GaN by polarization controlled FTIR absorption measurements. Methods for determining the orientation and the density of N-H bonds in defect complexes from mid-infrared absorption will be discussed.

A bulk GaN crystal was grown by the ammonothermal method on a (1128) hydride vapor phase epitaxy (HVPE) seed using basic chemistry.2,12 A sample for absorption measurements was cut from the grown crystal along the m-plane, thus allowing IR transmission experiments with E||c and E||a (or any angle between the c and a axes). The sample was thinned to a thickness of 450 μm and polished on both sides to optical quality. No dark lines indicative of polishing damage were observed by cathodoluminescence measurements. Secondary ion mass spectrometry (SIMS) was used to determine [O], [C], [Na], and [H] of 2 × 10¹⁷ cm⁻³, 2 × 10¹⁷ cm⁻³, 2 × 10¹⁷ cm⁻³, and 5 × 10²⁰ cm⁻³, respectively.

Infrared absorption spectra were measured on a 1 mm diameter spot at normal incidence with a commercial FTIR spectroscopy system (Nicolet Magna 850) using a KBr beam splitter and a KBr detector at room temperature. Resolution of 0.1 cm⁻¹ and linearly polarized light was used for all measurements. A holographic wire grid polarizer with an extinction ratio of >200 was used in front of the sample to control the polarization angle of the incident light. A free carrier concentration (FCC) of approximately 1.5 × 10¹⁸ cm⁻³ was determined from the IR reflection spectrum.22

Figure 1(a) shows the transmittance of the sample with incident light polarization along the c- (E||c) and the a-axes (E||a). Transmittance calculated from the dielectric function of GaN using the Drude model and the measured FCC is

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shown in dashed red. The sharp absorption peaks observed in the measured spectrum between 3000 and 3250 cm\(^{-1}\) correspond well with previous experimental reports and the calculated stretch vibration frequencies of V\(_{Ga}\)-H complexes. Broader absorption peaks at around 3350 cm\(^{-1}\) have not been previously reported from GaN. As [O] of the sample is in the order of \(1 \times 10^{19}\) cm\(^{-3}\), these peaks originate most likely from O-H complexes, which have stretch modes at around 3400 cm\(^{-1}\) in SnO\(_2\) and around 3600 cm\(^{-1}\) ZnO. The stretch modes of most other possible complexes of O, C, and H in GaN are located at frequencies lower than 3000 cm\(^{-1}\). No absorption peaks were detected from a reference \(m\)-plane HVPE sample with FCC of \(4.4 \times 10^{17}\) cm\(^{-3}\) (data not shown). 

The absorption coefficient of the peaks in the 3000–3500 cm\(^{-1}\) range was determined by using the calculated transmittance spectrum as a baseline and shown in blue in Fig. 1(b) for E||c and E||a. Twelve peaks can be identified and are labeled as I–XII. The position, full width half maximum (FWHM), and intensity of the peaks were determined by fitting 12 Gaussian peaks using a Monte Carlo algorithm. The fitted curves of E||c and E||a absorbance spectra are shown in red in Fig. 1(b).

The absorption coefficients of peaks I–XII were calculated from the Gaussian peak fitting of the absorption spectra measured with incident light polarization axis rotated 360° in 11.25° intervals from the c-direction. The resulting absorption coefficients of the fitted peaks are shown as blue dots in Fig. 2. No change in the FWHM or position of the peaks was observed with the rotation of the incident light polarization axis. As can be seen from Fig. 2, the angular intensity dependency of the absorption peaks can be divided into three groups: maximum absorption along the c-axis (Type 1), maximum along the a-axis (Type 2), and no dependency. The properties of the peaks are summarized in Table I.

The intensity of light (I) absorbed by an electric dipole in a semiconductor material can be written as

\[
I \propto \sum_{R_{k} \in C_{0}} |e \cdot (R_{k}d)|^2, \tag{1}
\]

where \(e\) is the polarization vector of the incident light, \(d\) is the transition dipole moment, and, in the case of GaN, \(R_{k}\) is the symmetry operator of the \(C_{4v}\) point group of hexagonal wurtzite structure. For bond stretch modes, the transition dipole moment needs to be aligned with the bond direction. Using Equation (1), the orientation of the absorbing bonds can be determined from the angular dependency of the absorption intensity.

The angular dependency of the absorption peaks shown in Fig. 2 can be understood by examining the alignment of hydrogen bonds in the hexagonal GaN lattice. In a gallium vacancy, three of the surrounding nitrogen atoms are related by symmetry, while the fourth is distinct. Thus, hydrogen bonds in a hydrogenated gallium vacancy can be divided into two groups: type A where the hydrogen atom is bonded with the distinct nitrogen atom and the N-H bond is aligned approximately along the c-axis, and type B where the hydrogen atom is bonded with one of the three nitrogen atoms. In the case of interstitial hydrogen, H in an AB-site bonds with a N atom approximately parallel (AB(N)||) or perpendicular (AB(N)\(\bot\)) to the c-axis, while in a BC site a H atom forms bonds with both N and Ga atoms parallel to the c-axis. The atom placement and N-H bonds in V\(_{Ga}\)-H\(_4\) and interstitial hydrogen are shown in Figure 3.

The angular dependency of the type 1 peaks (I, VII, and IX) correlates well with the calculated absorption of a single type A bond (red curves in Fig. 2, peaks I, VII, and IX). The frequencies of peaks I and VII are in agreement with the calculated stretch frequencies of type A N-H bonds in V\(_{Ga}\)H\(_{1,2,3}\). Compared with peak I, the broader FWHM of peak VII suggests that it originates from several closely spaced stretch modes of V\(_{Ga}\)-H\(_4\) complexes with different levels of hydrogenation or charge state. The calculated stretch frequencies of V\(_{Ga}\)H\(_{1,2,3}\) complexes with type A bonds deviate only 3 cm\(^{-1}\) from each other which can explain the observed broadening. The frequency of peak IX matches the calculated stretch frequency of BC\(\parallel\) hydrogen and to some extent V\(_{Ga}\)H\(_{4}\). As the V\(_{Ga}\)H\(_{4}\) complex should be
TABLE I. Absorption peak properties. Type 1 and type 2 denote maximum absorption with incident light polarization axis parallel to the c- and a-axis, respectively. Approximate concentration of N-H bonds and hydrogenated vacancies are listed for the peaks associated with V\textsubscript{Ga}-H.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Position (cm\textsuperscript{-1})</th>
<th>FWHM (cm\textsuperscript{-1})</th>
<th>Polarization dependency</th>
<th>Proposed origin</th>
<th>N-H bond concentration (cm\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>3150</td>
<td>8</td>
<td>Type 1</td>
<td>V\textsubscript{Ga}-H\textsubscript{3}</td>
<td>5.1 \times 10\textsuperscript{17}</td>
</tr>
<tr>
<td>II</td>
<td>3164</td>
<td>8</td>
<td>Type 2</td>
<td>V\textsubscript{Ga}-H\textsubscript{2}</td>
<td>3.4 \times 10\textsuperscript{17}</td>
</tr>
<tr>
<td>III</td>
<td>3175</td>
<td>8</td>
<td>Type 1/2</td>
<td>V\textsubscript{Ga}-H\textsubscript{1,2}</td>
<td>2.6 \times 10\textsuperscript{17}</td>
</tr>
<tr>
<td>IV</td>
<td>3188</td>
<td>11</td>
<td>Type 1 + 2</td>
<td>V\textsubscript{Ga}-H\textsubscript{2}</td>
<td>1.5 \times 10\textsuperscript{18}</td>
</tr>
<tr>
<td>V</td>
<td>3203</td>
<td>11</td>
<td>Type 2</td>
<td>V\textsubscript{Ga}-H\textsubscript{1,2}</td>
<td>5.1 \times 10\textsuperscript{17}</td>
</tr>
<tr>
<td>VI</td>
<td>3219</td>
<td>12</td>
<td>Type 2</td>
<td>V\textsubscript{Ga}-H\textsubscript{1,2,3}</td>
<td>9.4 \times 10\textsuperscript{17}</td>
</tr>
<tr>
<td>VII</td>
<td>3234</td>
<td>13</td>
<td>Type 1</td>
<td>V\textsubscript{Ga}-H\textsubscript{1,2}</td>
<td>1.6 \times 10\textsuperscript{18}</td>
</tr>
<tr>
<td>VIII</td>
<td>3255</td>
<td>225</td>
<td>None</td>
<td>Defect clusters</td>
<td>...</td>
</tr>
<tr>
<td>IX</td>
<td>3320</td>
<td>6</td>
<td>Type 1</td>
<td>O-H or BC\textsubscript{1} H</td>
<td>...</td>
</tr>
<tr>
<td>X</td>
<td>3324</td>
<td>6</td>
<td>Type 2</td>
<td>O-H</td>
<td>...</td>
</tr>
<tr>
<td>XI</td>
<td>3347</td>
<td>10</td>
<td>Type 2</td>
<td>O-H</td>
<td>...</td>
</tr>
<tr>
<td>XII</td>
<td>3382</td>
<td>59</td>
<td>None</td>
<td>Defect clusters</td>
<td>...</td>
</tr>
</tbody>
</table>

Unstable in GaN\textsuperscript{10}, peak IX originates most likely from BC\textsubscript{1} hydrogen. Other possible origin is an O-H bond aligned with the c-axis.

The calculated absorption of the type B N-H bonds can be matched to the angular dependency of the type 2 peaks (red curves in Fig. 2, peaks II, V, VI, X, and XI). The frequency of peak II matches well the calculated stretch frequencies of a V\textsubscript{Ga}-H\textsubscript{3} complex with type B bonds\textsuperscript{9,10} and its narrow line-width suggest a single origin. The frequencies of peaks V and VI match well the calculated frequencies of V\textsubscript{Ga}-H\textsubscript{2,3} with type B bonds\textsuperscript{9,10} and the broad FWHM of both peaks suggests several closely spaced stretch modes. The FWHM of peak IX is very narrow and the frequency matches well the calculated frequency V\textsubscript{Ga}-H\textsubscript{4} complex but also lies in the frequency range of O-H bonds. The equal line-width and maximum intensity together with the close spacing (4 cm\textsuperscript{-1}) of peaks IX and X suggest a similar origin, most probably O-H, only with different bond orientation.

Peak IV shows the strongest absorption and a good angular dependency fit can be obtained with a combined absorption of one type A and two type B N-H bonds (red curve in Fig. 2, peak IV). The frequency of peak IV matches well the calculated stretch frequencies of a V\textsubscript{Ga}-H\textsubscript{3} complex\textsuperscript{9,10}. The calculated stretch frequencies of type A and type B N-H bonds in a V\textsubscript{Ga}-H\textsubscript{3} complex differ only by 3 cm\textsuperscript{-1} and the close stretch frequency spacing of type A and type B bonds may well lead to merging of the absorption peaks and results in mixed type 1 and 2 angular dependency. The N-H bond structure in a V\textsubscript{Ga}-H\textsubscript{3} complex and the broad FWHM of peak IV further supports this conclusion. Additionally, as the activation energy of type A and type B N-H bonds in a V\textsubscript{Ga}-H\textsubscript{3} complex is almost the same, a H atom could switch between the type A and type B bonds of a defect complex depending on the incident light polarization.

The intensities of peaks III, VIII, and XII show no dependency on incident light polarization suggesting they originate from randomly oriented N-H or O-H bonds in defect clusters which break the crystal symmetry. This is supported by the large FWHM of peaks VIII and XII. However, the FWHM of peak III is equal to that of peaks I and II associated with V\textsubscript{Ga}-H\textsubscript{2} and V\textsubscript{Ga}-H\textsubscript{3} and is thus likely from a single N-H stretch mode. The frequency of peak III is close to the calculated stretch frequencies of type A and B bonds in V\textsubscript{Ga}-H\textsubscript{1,3} and V\textsubscript{Ga}-H\textsubscript{2,9,10}. The flat angular response can be obtained assuming similar merging of type A and type B stretch modes as with peak IV, but with a type A to B bond ratio of 1:3 (red curve in Fig. 2, peak III). However, the possibility of a randomly orientated N-H bond cannot be ruled out.

As the stretch frequencies of V\textsubscript{Ga}-H with different levels of hydrogenation and charge state overlap, unambiguous peak assignment based on the data presented here is not possible. However, FTIR data measured at temperature of 4.2 K from a c-plane ammonothermal sample with a comparable FCC show clear absorption corresponding to peaks IV, V, and VI observed here, but no absorption at frequencies close to peaks II and III is seen\textsuperscript{6}. As all peaks II–VI have contribution from type B N-H bonds they should be detectable also from a c-plane sample. As this is not the case, the origin of peaks II, III, and IV–VI must be different. Based on this, the proposed origins of all peaks observed here are listed in Table I. The proposed peak assignment indicates a deviation of 20–50 cm\textsuperscript{-1} (1%–2%) between the calculated stretch frequencies\textsuperscript{9,15} and the measured ones. This is within the reported uncertainty of 5% of the calculated values\textsuperscript{9}.
The bonded hydrogen content $C_H$ of an absorption peak of an N-H stretch mode can be evaluated from

$$C_H = \frac{1}{\sigma} \int A(\omega) d\omega,$$

(2)

where $\sigma$ is the absorption cross section of the N-H bond and $A(\omega)$ the absorbance at the photon frequency $\omega$. A literature value obtained by resonant nuclear reaction analysis was used for $\sigma$. The N-H bond concentrations calculated by Equation (2) are listed in Table I for peaks associated with $V_{Ga^2}$.

The $V_{Ga^2}$-H defect concentration can be approximately determined from the type A bond concentration. Assuming that the formation energy of a $V_{Ga^3}$-H defect complexes with and without a type A bond is equal, their density should thus also be equal. By using type A bond density of $5.1 \times 10^{17}$ cm$^{-3}$ determined from peak I, the total density of $V_{Ga^2}$-H$_3$ defects is approximately $1 \times 10^{18}$ cm$^{-3}$. In a similar manner, the $V_{Ga^2}$-H$_2$ density of approximately $3 \times 10^{18}$ cm$^{-3}$ can be determined from peak VII and the total density of $V_{Ga^2}$-H$_4$ defects in the sample is approximately $4 \times 10^{18}$ cm$^{-3}$. This is well in line with positron annihilation measurements of ammonothermal GaN, which have showed a total $V_{Ga^2}$-H concentration of $5 \times 10^{17}$ cm$^{-3}$ with main contribution from $V_{Ga^2}$-H$_1$. The high oxygen donor concentration ($1 \times 10^{15}$ cm$^{-3}$), it is likely that all acceptor type vacancy complexes exist in negatively charged state. The obtained acceptor type $V_{Ga^2}$-H$_4$ concentration of approximately $3 \times 10^{18}$ cm$^{-3}$ can largely explain the observed room temperature FCC of $1.5 \times 10^{18}$ cm$^{-3}$.

Based on our results, FTIR absorption measurements can be used to quickly and non-destructively evaluate the hydrogenated defect density and to some extent identify defect types on a free standing GaN wafer. The small spot size allows mapping the defect distribution. The only requirements for the sample are both side optical polish and FCC below approximately $5 \times 10^{18}$ cm$^{-3}$, as otherwise FCC absorption will mask the N-H peaks in the 3000–3500 cm$^{-1}$ range. It should be noted that unlike positron annihilation spectroscopy, absorption based methods can detect also electrically passive $V_{Ga^2}$-H$_1$, $V_{Ga^2}$-H$_2$, and positively charged $V_{Ga^2}$-H$_4^+$ in GaN.7

In summary, hydrogenated defect complexes were analyzed by polarization controlled FTIR absorption measurements in ammonothermal GaN. A majority of the absorption peaks were associated with $V_{Ga^2}$-H$_{1,2,3}$ complexes, but also possible hydrogenated oxygen defect complexes and hydrogen in BC sites were detected. Lattice direction independent absorption was associated with defect clusters with no crystalline symmetry. The absorption peak intensity was used to determine a total $V_{Ga^2}$-H density of approximately $4 \times 10^{18}$ cm$^{-3}$, with main contribution from $V_{Ga^2}$-H$_{1,2}$. Also, a significant concentration of electrically passive $V_{Ga^2}$-H$_3$ defects was detected. The high density of hydrogenated defect complexes is expected to affect the structural, optical, and electrical properties of ammonothermal GaN crystals.

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