Localized vibrational modes of carbon-hydrogen complexes in GaN

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Localized vibrational modes of carbon-hydrogen complexes in metalorganic chemical vapor deposition grown GaN on sapphire were studied using a Fourier-transform infrared spectroscopy technique. Three distinctive localized vibrational modes were observed around 2850, 2922, and 2959 cm^{-1} for undoped, Si-, and Mg-doped samples. These peaks are related to CH, CH$_2$, and CH$_3$ defect complexes, respectively. However, the localized vibrational modes were not observed in some undoped samples, which is indicative of high quality grown epitaxial layers. It is also observed that the frequencies and intensities of the localized vibrational modes are sample dependent. © *1999 American Institute of Physics.* [S0003-6951(99)00831-1]

The development of III–V nitride semiconductors and the emerging advances in a broad range of nitride-based electronic and optoelectronic devices have witnessed dramatic successes in recent years. One of the most important aspects of recent investigations of III–V nitrides is the ability to produce and fairly control *n*- and *p*-type doped materials. Massive research efforts on devices have been launched after Amano *et al.*[1] observed cathodoluminescence results from Mg-doped GaN. However, the dopant incorporation remains the subject of various investigations. The localized vibrational modes (LVMs) spectroscopy is a very powerful tool in identifying impurities and dopant incorporation in semiconductors. This is due to the fact that the LVMs spectroscopy is very sensitive to the atomic structure surrounding a dopant atom, the dopant location, dislocation density, and strain. As a typical example, the high-resolution LVMs spectrum of a substitutional acceptor carbon in GaAs exhibits a fine structure due to the Ga isotopic effect.[2]

The LVMs spectroscopy has not been employed aggressively in studying dopants incorporation and impurities in GaN and related compounds. One of the major problems associated with the study of the LVMs in GaN is that the substrate used to grow GaN is sapphire, which has a very strong infrared absorption band in the spectral region of 450–1500 cm^{-1}. This band obscured many LVMs of simple substitutional impurities and dopants such as Mg, C, and Si. Hydrogen related defect complexes usually possess LVMs at frequencies higher than 1500 cm^{-1}. Hence, it is possible to study dopants incorporation in GaN by monitoring the dopant-H complexes related LVMs. As an example, hydrogen can passivate Mg, which is an important acceptor in GaN. Hydrogen can be easily incorporated into III–V nitrides during or after the growth of the materials.[3] Additionally, atomic hydrogen can easily diffuse into the III–V nitrides during device processing, since most of the chemicals that come into contact with the surface contain hydrogen.

In this letter, we report on the LVMs of carbon-hydrogen complexes in doped and undoped metalorganic chemical vapor deposition (MOCVD) GaN grown on sapphire substrate. The C–H LVMs were observed in samples doped with Mg, Si, or contaminated with O$_2$ and in undoped samples. However, these LVMs were not observed in undoped high quality samples as judged by the photoluminescence spectra. This suggests that the carbon is incorporated during the growth in the relatively lower quality samples. It is also observed that the frequencies and the intensities of the C–H LVMs are sample dependent, perhaps due to the variation of the dislocation densities and strains in the samples.

All the GaN samples tested in the present investigations were grown on sapphire substrates by the MOCVD technique at 1050 °C. The thickness of the GaN thin films ranged from 1 to 2.5 μm. The localized vibrational modes were measured at 77 K using a BOMEM Fourier-transform infrared spectrometer in conjunction with a continuous flow cryostat. Many samples were tested, but nine samples were selected for this study. Some of their characteristics are described in Table I. A special sample holder was constructed so that the incident light from the spectrometer

TABLE I. Characteristics of the samples used in the present study. The carrier concentration and mobility were measured at 300 K. The undoped samples are *n*-type with a typical concentration of $(1-8)\times10^{17}$ cm^{-3}.

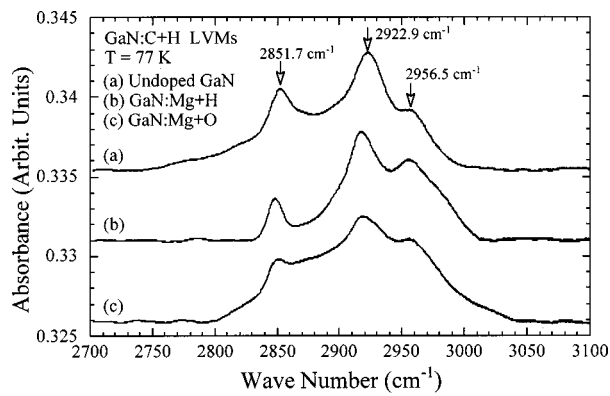| Sample	Dopant	Contaminant	Carrier gas	Carrier concentration ($\times10^{17}$ cm^{-3})	Mobility (μ) (cm^2/V s)
A	undoped		H$_2$	7.0	53.0
B	Mg		H$_2$	3.4	24.0
D	Mg	O$_2$	H$_2$	12.0	
E	undoped	O$_2$	N$_2$		
F	undoped		H$_2$		
G	Si		H$_2$	12.3	350
J	Si		H$_2$	6.0	375
K	undoped		H$_2$	3.0	400.0
L	undoped		H$_2$	0.3	150.0

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FIG. 1. Carbon-hydrogen localized vibrational mode spectra of GaN samples A, B, and D measured at 77 K. Spectra (a), (b), and (c) were obtained for undoped sample (A), Mg-doped sample (B), and Mg-doped and O$_2$ contaminated sample (D), respectively. Hydrogen was used as a carrier gas during growth for the three samples.

reached the sample at the Brewster's angle. This configuration proved to be very useful to avoid the interference patterns generated from the substrate as well as from the GaN epitaxial thin layers. The LVMs were obscured by the interference patterns in spectra collected at the normal incident configuration.

The three spectra shown in Fig. 1 were measured for samples A, B, and D (see Table I). It is clear that three distinctive peaks are observed at 2851.7, 2922.9, and 2956.5 cm^{-1}. The intensity of the three peaks are sample dependent. The shapes of the spectra indicate that there are contributions from other LVMs, especially around 2900 cm^{-1}, in good agreement with previously published results[4] for C–H LVMs in vapor phase epitaxial GaN:Mg. Additional C–H LVMs spectra are plotted in Fig. 2. The spectra in Fig. 2 were obtained for samples E, F, and G, which are contaminated with O$_2$ [spectrum (a)], undoped [spectrum (b)], and Si-doped GaN [spectrum (c)], respectively. Figure 3 shows a spectrum obtained for a Si-doped GaN sample J. The shape of the spectrum in this figure is somewhat different than the spectrum observed for the Si-doped sample (G) in Fig. 2 [see spectrum (c)]

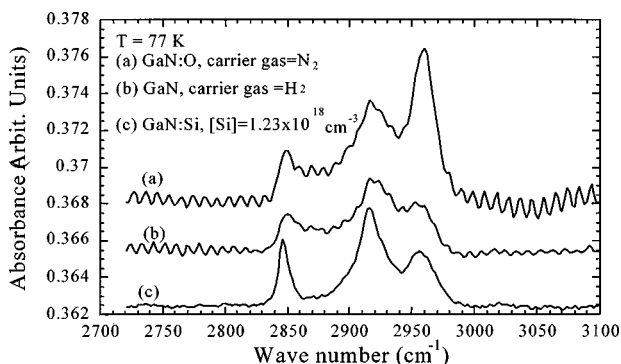Many of the doped and undoped samples obtained from

FIG. 2. Carbon-hydrogen localized vibrational mode spectra of GaN samples E, F, and G measured at 77 K. Spectra (a), (b), and (c) were obtained for undoped but O$_2$ contaminated sample (E), undoped sample (F), and Si-doped sample (G), respectively. The carrier gas for sample (E) was N$_2$.
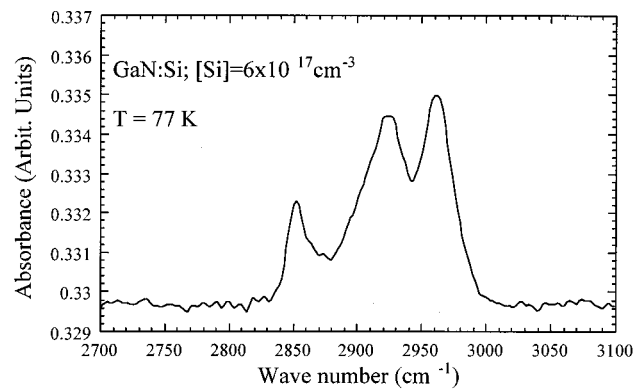

FIG. 3. Localized vibrational mode spectrum of CH complexes in Si-doped sample (J) measured at 77 K. The shape and the intensity of the peaks are different than the results reported in Figs. 1 and 2.

different sources were tested and found to contain the C–H LVMs. However, there were a few samples that do not show these LVMs. An example is shown Fig. 4, where two spectra of undoped samples are recorded at the normal incident configuration. The spectra are sloped due to the interference from the thin layers. The interference from the substrate in sample (K) [spectrum (a)] was not observed because the substrate backside was not polished. On the other hand, the interference from the substrate in sample (L) [spectrum (b)] is not large enough to cause any problems in the spectral region shown in the figure. This may be due to the fact that the substrate was polished at an angle (slightly wedged). It was observed that samples which do not exhibit C–H LVMs (see Fig. 4) possess the characteristic of narrower photoluminescence peaks near the band edge (free or neutral donor bound excitons' peaks) as compared to those of samples with C–H LVMs.

By careful inspection of Figs. 1–4, we observed that the intensity and the shape of the three dominant C–H LVMs in GaN are independent of the dopants, contaminants, and carrier gas. They are observed in both doped and undoped samples. However, undoped samples with narrow photoluminescence peaks near the band edge do not show the C–H LVMs. The full width at half maximum of the three peaks are also sample independent. Additionally, the intensities of the peaks are independent of the various dopants concentrations in agreement with Brandt *et al.*[5] For example, spectrum (c) in Fig. 2 is obtained for a Si-doped sample with [Si]
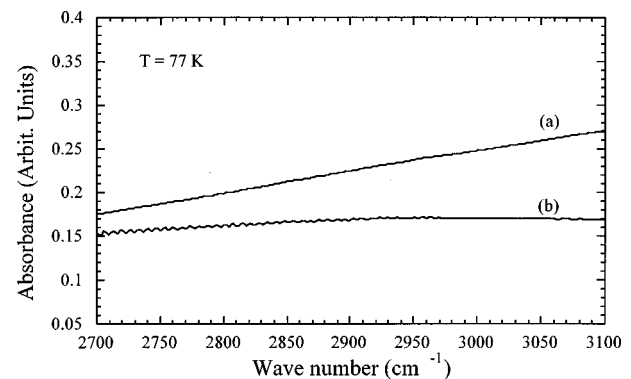

FIG. 4. Absorbance spectra of samples K [spectrum (a)] and L [spectrum (b)] measured at the normal incident configuration. These samples do not exhibit C–H complex related localized vibrational modes.

$= 1.23 \times 10^{18}$ cm^{-3}, while the spectrum in Fig. 3 is obtained for a Si-doped samples with $[Si] = 6.0 \times 10^{17}$ cm^{-3}. Yet, the intensities of the peaks in Fig. 3 are larger than those of spectrum (c) in Fig. 2. It is tempting to explain this behavior in terms of H trapping competition between C and Si substitutional atoms in GaN, but the results from other samples do not support this premise.

The three LVM peaks in the spectra in Fig. 1 observed at 2851.7, 2922.9, and 2956.5 cm^{-1} where tentatively assigned[4] to the CH stretching mode, CH$_2$ asymmetric stretching mode, and CH$_3$ asymmetric stretching mode, respectively. This assignment is based on a comparison between the LVM measurements in GaN and the calculated C–H frequencies[6] in α-Si$_{1-x}$C$_x$:H. However, we noted that the frequencies of the three peaks are sample dependent. It was found that the CH frequency could vary in different samples between 2847.0 and 2853.0 cm^{-1}, the CH$_2$ mode varies between 2910.0 and 2924.0 cm^{-1}, and the CH$_3$ mode varies between 2955.0 and 2963.0 cm^{-1}. The sample dependency of the LVM frequencies could be explained as follows. The typical dislocation densities in GaN are about $10^8 - 10^9$ cm^{-3}. Hence, the atomic structures surrounding the C–H defect complexes are affected by the dislocations, which produce local strains. The strains associated with dislocations are usually sample dependent. These strains obviously affect the LVMs in a way that their frequencies are sample dependent.

It is believed that the H complexes in GaN are thermally more stable than in other semiconductor hosts.[7] The hydrogen and carbon in the present samples are incorporated during growth since the samples were not subject to any other processes. Hydrogen is well known to passivate dopants and impurities in semiconductors. For example, the hole compensation and the amount of incorporated H as a function of Mg concentration in GaN:Mg suggest the passivation of Mg by hydrogen.[8–10] However, the LVMs of Mg–H complexes in GaN have not been observed in the present GaN:Mg samples. On the other hand, Brandt *et al.*[5] reported two LVM peaks in the Raman and infrared spectra around 2168 and 2219 cm^{-1}, which were attributed to Mg–H LVMs. These frequencies, however, are not typical of Mg–H bonds.[7,11–13] They may be related to Si–H LVMs. But even with Si-doped samples (see Table I and Figs. 2 and 3), LVMs were not observed in the present investigation for either Mg–H or Si–H complexes.

With all samples (obtained from many sources) that were tested, only those with high quality photoluminescence spectra do not show the presence of C–H complexes related LVMs (see Fig. 4). We even tested the spectrometer for any possible contamination of hydrocarbons by running absorbance spectra without samples, with sapphire substrates, and with GaAs samples. It is clear, however, that the intensities and the line shape of the LVMs of the C–H complexes in GaN are sample dependent. Additionally, carbon incorporation and the formation of C–H complexes have proven to be difficult for one to reach a concrete conclusion. Thus, further studies are needed to control doping and H passivation in GaN.

In conclusion, we presented localized vibrational mode spectra related to C–H complexes in MOCVD GaN. The C–H localized vibrational modes were observed in undoped, Si- and Mg-doped GaN. The shape and the peak positions of these LVMs were found to be sample dependent. The sample dependency was explained in terms of local strains generated from the high dislocation densities inherited in GaN samples. The C–H LVMs, however, were not observed in samples that exhibit photoluminescence spectra with narrow band edge peaks. Three distinctive LVM peaks observed around at 2851, 2922, and 2956 cm^{-1} where assigned to CH, CH$_2$, and CH$_3$ stretching modes, respectively. The CH$_2$ asymmetric frequency mode was found to vary the most in various doped and undoped samples. Localized vibrational modes associated with Si- and Mg-doped GaN were not observed in the current study. Additional LVM investigation is needed to understand the dopant incorporation and H passivation in III nitrides.

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