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Local vibrational modes in Mg-doped gallium nitride

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Four local vibrational modes are reported for Mg-doped wurtzite GaN, which as grown possesses high concentrations of hydrogen. The modes, studied by Raman and infrared absorption spectroscopy appear to form two pairs. Based on the observed selection rules, one pair, with room-temperature frequencies of 2168 and 2219 cm^{-1} is assigned to inequivalent Mg-H complexes in the c plane and parallel to the c axis, respectively. The origin of the second pair of modes at 2151 and 2185 cm^{-1}, which are IR inactive, is speculatively linked to the presence of diatomic molecules such as N_2 or H_2.

Wide-band-gap II-VI and III-V semiconductors are receiving considerable attention due to their possible applications in ultraviolet to green-light emission devices and high-temperature electronics. A major obstacle to the realization of such devices is an apparent difficulty to obtain p-type doping in these materials when using growth techniques such as metal-organic chemical vapor deposition (MOCVD). This limitation has recently been overcome by the successful growth of films by molecular-beam epitaxy (MBE). The absence of hydrogen from the gas phase during MBE growth has led to the assumption that the formation of acceptor-hydrogen complexes is the reason for the low doping efficiency in MOCVD-grown material.

Dopant-hydrogen complexes in semiconductors have been studied with a variety of techniques.[1] The effect of hydrogen on the electrical activity of the dopants has been studied by temperature-dependent Hall effect measurements and the spatial extent of a passivation by capacitance-voltage measurements. A definite proof for the existence of complexes, however, can only be obtained by the observation of their local vibrational modes (LVM) with infrared (IR) or Raman spectroscopies. In silicon and gallium arsenide, where the effects of hydrogen have been most extensively studied so far, the local vibrational modes of hydrogen bound to a large variety of dopants have been identified. These include H-containing complexes with B, Al, Ga, P, As, and Sb in Si and with Si, Ge, Sn, Zn, Be, and Cd in GaAs.[2,3] By analyzing the polarization dependence of vibrational modes in IR and Raman experiments, information on the symmetry of the complexes is obtained. Calculations determining the total energy of different configurations that are compatible with the observed symmetry or measurements of the vibrational modes under uniaxial stress can then identify the microscopic structure of the complexes.

In ZnSe, a wide-band-gap compound, the observation of the vibrational modes of N-H complexes in MOCVD grown material has indeed shown that such acceptor-hydrogen complexes are formed and appear to limit the p-type doping efficiency.[4,5] In p-type GaN electrical measurements have shown that Mg acceptors can be passivated or compensated by introduction of hydrogen from a remote microwave plasma at hydrogenation temperatures above 400 °C.[6,7] A new photoluminescence line at 3.35 eV was observed after hydrogenation, which might indicate that hydrogen has a donor level in this material. On the other hand, secondary-ion mass spectrometry (SIMS) revealed that hydrogen can be introduced to the same concentrations as the Mg acceptors, which could indicate complex formation. Vibrational spectroscopy, as discussed above, should be able to establish the presence and structure of such hydrogen-dopant complexes. In this paper, we report the observation of several local vibrational modes in Mg-doped GaN epitaxial films which possess significant H concentrations. We assign a LVM pair at 2168 and 2219 cm^{-1} to the stretching vibrations of two inequivalent Mg-H complexes. The origin of a second, IR inactive pair at 2151 and 2185 cm^{-1} is discussed and might be due to the presence of H_2 or N_2 in the films.

Wurtzite GaN epilayers were grown on (0001) c-plane sapphire substrates by electron cyclotron resonance (ECR) microwave plasma assisted MBE.[8,9] Gallium and magnesium were evaporated from conventional Knud-

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sen cells, and activated nitrogen was produced with an efficiency of about 10% by passing molecular nitrogen through the ECR source at a pressure of 10^{-4} Torr and a microwave power of typically 35 W in the ECR plasma. Prior to the growth of the GaN epilayer, the substrates were exposed to the N plasma for 30 min to convert the surface of the sapphire substrates to AlN. A GaN buffer layer was then grown at 500 °C followed by the high-temperature growth of the actual film at 800 °C at a growth rate of 200 to 250 nm/h. The two-temperature growth was shown to promote lateral growth and thus layer-by-layer growth. Depth profiles from SIMS typically show Mg concentrations of 10^{20} cm^{-3}. Room-temperature Hall measurements find hole concentrations of up to 10^{19} cm^{-3} in some samples, which corresponds to a doping efficiency of $\approx$10%. However, the specific samples studied here show H concentrations above 10^{19} cm^{-3} as determined with SIMS. The exact origin of this contamination is unknown at present, but appears correlated with the microwave power used in the ECR source and linked to the Mg doping. The ECR plasma tends to activate spurious hydrogen concentrations in the gas phase and thereby increases its incorporation probability in the films. Furthermore, there is mass-spectroscopic evidence from the outgassing Mg source that Mg tends to getter hydrogen which is then released during the Mg evaporation. The hydrogen content in the films can be minimized by carefully outgassing of the system prior to the growth of the GaN films, thereby increasing the doping efficiency. MOCVD-grown Mg-doped GaN was not available for this study.

Raman spectra were excited at room temperature by 100 mW of 488 nm laser light in a custom-built Raman microprobe based on an Olympus metallurgical microscope with a 50× objective ($NA = 0.8$). The spot size was approximately 2 μm. Spectra were detected by an imaging PMT (1024×1024) with a holographic notch filter (Kaiser Optical Systems) and a 640 nm spectrograph with a 1200 groove/mm grating. Typical collection times were between 200 and 800 s. The spectral resolution was 4 cm^{-1} and the precision of the line center determinations is ± 1 cm^{-1}. Polarized spectra were corrected for differences in grating efficiency by calibration with a white light source. Since only epilayers of typically 1 μm thickness grown on c-plane sapphire were available for this study, only Raman measurements in the backscattering configuration $z(xx)\bar{z}$ or $z(xy)\bar{z}$ could be performed, with the z direction parallel to the c axis of the wurtzite structure.

The infrared absorption measurements were conducted at temperatures of 300 K and 8 K with a Bruker IFS 113 Fourier transform spectrometer. A mid-IR glowbar light source, a KBr/Ge beam splitter, and an MCT detector were used. The resolution was 2 cm^{-1}. To avoid reduction of sensitivity due to light interference in the thin GaN layers, the light was incident on the samples at an angle of 60° from the surface normal. For an index of refraction corresponding to a relative permittivity of ≈ 9, the infrared light propagation vector made an angle of 15° with respect to the c axis. Because of the sample geometry, only transmission measurements with the propagation of the light nearly parrallel to the c axis could be performed.

The results of the room-temperature Raman and infrared absorption measurements on a variety of Mg-doped GaN samples are summarized in Fig. 1. Four Raman active vibrational modes were detected, which appear to comprise two pairs. One sample shows only the first pair at 2168 and 2219 cm^{-1} [Fig. 1(a)]. In most samples studied, however, a second pair at about 2151 and 2185 is observed as shown in the Raman spectra of Fig. 1(b), the lower frequency peak being considerably broader than the other peaks observed here. Within a pair, the relative intensities of the peaks remain constant at around 1 to 2 for both pairs, while the intensities of the two pairs with respect to each other vary considerably as exhibited by the two Raman spectra shown. Both pairs show the same polarization dependence: By changing from the $z(xx)\bar{z}$ to the $z(xy)\bar{z}$ scattering configuration, the Raman intensity is reduced by a factor of 10, but the spectral shape remains unchanged. Both undoped and hydrogenated Si-doped (4×10^{20} cm^{-3}) control samples were investigated for similar vibrational modes both in this frequency region and near 3000 cm^{-1}. No Raman signal of a local vibrational mode was found in these samples.

In the IR absorption of all Mg-doped GaN films studied here, however, only the first pair is observed, with the high-frequency mode at 2219 cm^{-1} barely detectable in the specific transmission geometry that was used. In fact, the IR spectrum shown in Fig. 1(c) was obtained on a

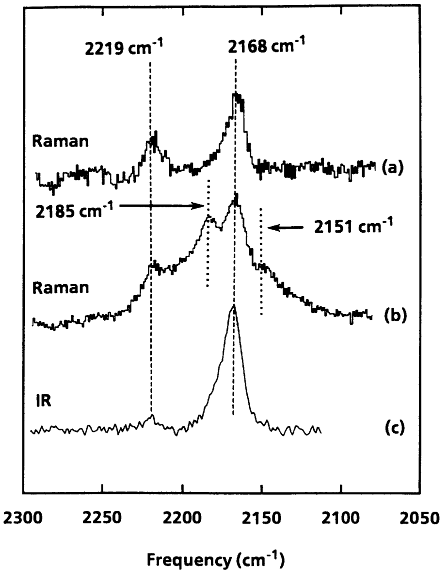

FIG. 1. Local vibrational modes in Mg-doped GaN. The Raman spectra (a) and (b) and the IR spectrum (c) were obtained from different samples. The Raman measurements were performed under ambient conditions in the $z(xx)\bar{z}$ polarization configuration. The IR measurements were performed with the sample in vacuum at room temperature. Two pairs of LVM are found, indicated by dashed and dotted lines. Only the pair at 2168 and 2219 cm^{-1} is IR active. It is assigned to Mg-H complexes oriented either in the c plane or parallel to the c axis of the wurtzite lattice, respectively.

sample possessing a particularly strong Raman signal at 2185 cm^{-1}, which is a constituent of the second pair. The typical linewidth of the 2168 cm^{-1} mode observed with both techniques is 15 cm^{-1}. This inhomogeneous broadening might be due to residual strain or the high concentration of vibrational centers.

Manabe and co-workers have studied local vibrational modes of Be in CdS and CdSe, which also have a wurtzite lattice.[10] While the wurtzite lattice has C_{6v} point group symmetry, the defect with Be on the Cd site has C_{3v} point group symmetry. The effect is a splitting of the local vibrational mode into two peaks with local symmetries A_1 (IR dipole parallel to c axis) and E_1 (IR dipole perpendicular to c axis). In the case of a hypothetical Mg-H local vibrational mode, the addition of the hydrogen changes the symmetry slightly. If the hydrogen atom is along the c axis bonding direction (e.g., Conf. I in Fig. 2), the point symmetry is C_{3v}. If, on the other hand, the H is along a bonding direction in the plane (e.g., Conf. II), the symmetry is C_s: there is a single plane of symmetry containing the Ga atom in the next layer and the Mg-H bond. This gives rise to the selection rules for infrared and Raman spectroscopies listed in Table I. For the specific transmission and scattering geometries employed here, we therefore expect from group theory to observe only vibrations of Conf. II (H in c plane) with IR, but both configurations in Raman.

Returning to the experimental results of Fig. 1, we find that the first pair at 2168 and 2219 cm^{-1} indeed behaves as expected for an acceptor-hydrogen complex in a wurtzite material. From the selection rule exhibited by the IR spectrum, we therefore would assign the 2168 cm^{-1} mode to the A' vibration of Mg-H complexes oriented in the c plane and the 2219 cm^{-1} mode to the A_1 vibration of Mg-H parallel to the c direction which is IR inactive for transmission experiments with the light propagating in the c direction. (The weak IR signal at 2219 cm^{-1} is indeed consistent with the slight off c axis orientation of the sample during the IR measurements.) This assignment to a H complex is corroborated by the SIMS results which show that the local vibrational modes are observable only in samples with $[\mathrm{Mg}] \geq 10^{20}$ cm^{-3} and, avaraged over the sample thickness, $[\mathrm{H}] \geq 10^{19}$ cm^{-3}. The participation of Mg in the complex is further supported by the absence of the modes discussed above in undoped or Si-doped GaN. Finally, the observed frequencies are in a spectral region where only stretching vibrations of hydrogen are expected. Indeed, the local vibrational modes of group-II–acceptor hydrogen complexes in p type GaAs and InP observed so far all lie between 2037 and 2287 cm^{-1}, very near to the modes reported here. However, there appears to be no previous report of vibrational modes related to Mg-H complexes in these materials.[11]

TABLE I. Selection rules for the vibrational spectroscopy of Mg-H complexes in wurtzite GaN.

	Point symmetry	Vibration	IR	Raman
Conf. I	C_{3v}	A_1	z	$xx = yy,\ zz$
Conf. II	C_s	A'	$x,\ y$	$xx,\ yy,\ xy,\ zz$

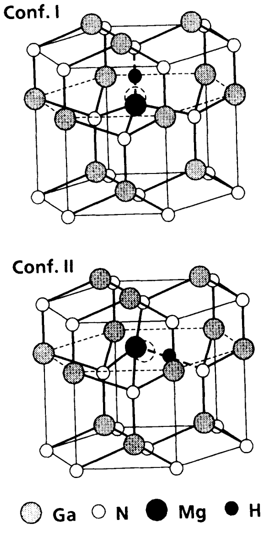

FIG. 2. Hypothetical structural configurations of the two inequivalent sites of the Mg-H complex in GaN. The hydrogen is assumed to be in a bond-center position, with the Mg atom relaxing to the plane formed by its nearest N neighbors. In Conf. I the Mg-H bond is in the c-axis direction, while in Conf. II the bond is in the c plane. The dashed circles indicate substitutional lattice sites.

The exact microscopic configuration of the Mg-H complex in GaN cannot be established from the measurements reported here, although the observed selection rules are consistent with the hydrogen situated on a Mg-N bond axis. There are two sites available: (i) the H in the Mg-N bond (bonding or bond-center site) or (ii) the H opposite to this bond in the antibonding site. Total energy calculations have determined that for both group-III acceptors in Si and for group-II acceptors in GaAs the bond center site is the energetically more favorable. This specific configuration is shown in Fig. 2 for the complex in both the c direction (Conf. I) and the c plane (Conf. II). The introduction of the hydrogen may lead to a threefold coordination of the acceptor atom and a relaxation towards the plane formed by its three nearest N neighbors. Support for this assumption might be obtained from the comparison of the observed stretching frequencies around 2200 cm^{-1} in GaN to those in corresponding molecules. One finds the stretching modes at 3444 cm^{-1} in NH_3 and 1450 cm^{-1} in MgH,[12] which could indeed indicate that both N and Mg participate in the bonding of the hydrogen atom. However, the corresponding argument fails in the case of B-doped Si, where the observed mode of the B-H complex has a lower frequency than both SiH_4 and B_2H_6. It should also be noted that the frequency of the proposed Mg-H local vibrational mode in GaN does not appear to be strongly influenced by the presence of nitrogen at the group-V lattice site, when compared, for example, to LVM's of group-II–acceptor hydrogen complexes in GaAs. This might indicate that the hydrogen atom is in the antibonding site rather than in the bond center position. In addition, in silicon the H-Ga complex has a local vibrational mode[13] at 2171 cm^{-1}, which coincides with the strong IR-active mode shown in Fig. 1. Therefore, another possible candidate for the complex is a nitrogen vacancy with one or several of the adjacent Ga atoms passivated by hydrogen. Since the LVM's are observed only in Mg-doped material, such a hypothetical vacancy should correlate with a Mg atom. Total energy calculation will be invaluable to identify the microscopic configuration(s) of the Mg-H complex in GaN.

The assignment of the second pair at 2151 and 2185 cm^{-1} in Mg-doped GaN films is considerably more difficult. The failure to observe absorption in IR spectroscopy would indicate that the microscopic structure does not exhibit a built-in dipole moment in the polarization direction of the IR used in the transmission experiments. (In fact, due to the limited signal-to-noise ratio, we can only conclude that the IR cross section is at least a factor of 20 smaller than that for the mode at 2168 cm^{-1}.) One possibility could be Mg_2 or Mg precipitates, although their vibrations are expected to occur at considerably lower frequencies. Another possibility are diatomics, however, H_2 and N_2 have stretching frequencies in the gas phase of 4395 and 2360 cm^{-1}, respectively. A definite assignment can once again only be made based on calculations. Although it is expected that the H_2 vibration in Si is considerably shifted downwards to about 2300 cm^{-1},[14] preliminary calculations of N_2 in GaN show that this molecule can be incorporated into the crystal without significant changes in its vibrational frequency.[15] The suggestion that the second pair might originate from N_2 molecules, again oriented in two nonequivalent configurations parallel to the c axis and in the c plane, receives some corroboration from the growth conditions used, which as in the case of GaAs, employed an overpressure of the group-V constituent to avoid surface segregation of Ga. It however remains to be understood under this assumption why the hypothetical N_2 mode is not observed in undoped or Si-doped GaN, which are grown with the same overpressure of nitrogen. One possibility is that the incorporation or stability of N_2 in GaN might be dependent on the Fermi level position. A continuing systematic study of growth conditions by LVM spectroscopy is anticipated to yield new insights and fundamental information on native defects as well as dopant incorporation during growth of GaN.

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[1] *Hydrogen in Semiconductors*, edited by J. I. Pankove and N. M. Johnson (Academic, San Diego, 1991).

[2] M. Stavola and S. J. Pearton, in *Hydrogen in Semiconductors* (Ref. 1), p. 139, and references therein.

[3] J. Chevallier, B. Clerjaud, and B. Pajot, in *Hydrogen in Semiconductors* (Ref. 1), p. 447, and references therein.

[4] J. A. Wolk, J. W. Ager III, K. J. Duxstad, E. E. Haller, N. R. Taskar, D. R. Dorman, and D. J. Olego, Appl. Phys. Lett. **63**, 2756 (1993).

[5] A. Kamata, H. Mitsuhasi, and H. Fujita, Appl. Phys. Lett. **63**, 3353 (1993).

[6] M. S. Brandt, N. M. Johnson, R. J. Molnar, R. Singh, and T. D. Moustakas, Appl. Phys. Lett. (to be published).

[7] S. Nakamura, N. Iwasa, M. Senoh, and T. Mukai, Jpn. J. Appl. Phys. **31**, 1258 (1992).

[8] T. D. Moustakas and R. J. Molnar, in *Semiconductor Heterostructures for Photonic and Electronic Applications*, edited by C. W. Tu, D. C. Houghton, and R. T. Tung, MRS Symposia Proceedings No. 281 (Materials Research Society, Pittsburgh, 1993), p. 753.

[9] T. D. Moustakas, T. Lei, and R. J. Molnar, Physica B **185**, 36 (1993).

[10] A. Manabe, A. Mitsuishi, H. Komiya, and S. Ibuki, Solid State Commun. **12**, 337 (1973).

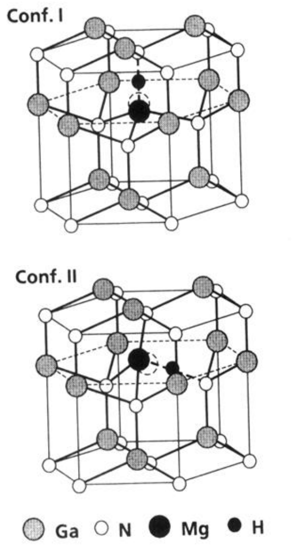
[11] R. Rahbi, B. Pajot, J. Chevallier, A. Marbeuf, R. C. Logan, and M. Gavand, J. Appl. Phys. **73**, 1723 (1993).

[12] A. Guntsch, Z. Phys. **104**, 587 (1937).

[13] M. Stavola, S. J. Pearton, J. Lopata, and W. C. Dautremont-Smith, Appl. Phys. Lett. **50**, 1086 (1987).

[14] C. G. Van de Walle, Phys. Rev. B **49**, 4579 (1994).

[15] J. Neugebauer and C. G. Van de Walle (private communication).



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