Local vibrational modes in Mg-doped GaN grown by molecular beam epitaxy

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Local vibrational modes in the region of the acoustic and optical phonons are reported for Mg-doped GaN grown by molecular beam epitaxy. The modes, studied by Raman spectroscopy, appear in addition to the known modes in the high-energy region around 2200 cm^{-1}. We suggest disorder-activated scattering and scattering from Mg-related lattice vibrations to be the origin of the low-energy modes. Our assignment is supported by calculations based on a modified valence-force model of Kane. Temperature-dependent measurements between 4 and 300 K exclude an electronic Raman-scattering mechanism. We also report a new line at 2129 cm^{-1} and discuss the origin of all five observed high-energy modes. © *1999 American Institute of Physics.*
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Magnesium is the only dopant known to achieve effective *p*-type doping in GaN. Mg-doped GaN is strongly compensated when grown under H-rich ambient conditions such as during metalorganic chemical vapor deposition (MOCVD). Hydrogen has been suggested to passivate the acceptor states and postgrowth treatment is necessary to obtain *p*-conducting material.[1,2] On the other hand, Mg-doped GaN grown by molecular beam epitaxy (MBE) is *p*-type in the as-grown state.[3] The hole concentration at room temperature is usually one or two orders of magnitude less than the Mg-concentration due to the high acceptor ionization energy and compensation effects.

The influence of Mg-doping on the lattice dynamics of GaN was previously studied by Brandt *et al.*[4] who found four local vibrational modes in MBE-grown Mg-doped GaN with frequencies of 2151, 2168, 2185, and 2219 cm^{-1}. They assigned the 2168 and the 2219 cm^{-1} peaks to stretching vibrational modes of two inequivalent Mg–H complexes, whereas the modes at 2151 and 2185 cm^{-1} were speculatively attributed to H$_2$ and N$_2$ vibrations, respectively. Alternatively, they suggested a H-decorated native defect as the lines origin. Based upon *ab initio* calculations Neugebauer and van de Walle found that Mg–H complexes are likely to form in GaN.[5] They claimed that hydrogen prefers the nitrogen antibonding sites and determined the frequency of the H stretch mode close to the value of the H stretch mode in NH$_3$ (3444 cm^{-1}). Götz *et al.*[6] assigned a vibrational mode at 3125 cm^{-1} in MOCVD-grown Mg-doped GaN to this kind of Mg$_{Ga}$–H complex. They supported their assignment by the observation of an isotopic shift after deuteration of their samples. The frequency of the suggested Mg$_{Ga}$–D vibration was determine as 2321 cm^{-1}. In contrast to their results, we found a peak at 2329 cm^{-1} in the spectra of different GaN samples but none at 3125 cm^{-1}. The line we observed at 2329 cm^{-1} originates from N$_2$ vibrations in air.[7] Whereas there is a busy discussion about the Mg-related high-energy modes, little is known about the influence of Mg-doping on the lattice dynamics in the region of the acoustic and optical phonons of the GaN host lattice.

The Raman experiments were carried out in backscattering geometry with a triple-grating spectrometer equipped with a cooled charge coupled device detector. The lines at 488, 514.5, and 568 nm of an Ar$^+$/Kr$^+$ mixed-gas laser were used for excitation. The line positions were determined with an accuracy better than 1 cm^{-1}. The temperature was varied between 4 and 300 K using an Oxford bath cryostat.

The samples under study were Mg-doped GaN films of about 1 μm thickness grown on sapphire (0001) substrates by MBE.[8] Samples A and B are *p*-conductive with a hole concentration at room temperature of 3.7×10^{17} and 1.4×10^{17} cm^{-3}, respectively, whereas the other two samples are compensated but *n*-conductive. Secondary ion mass spectroscopy (SIMS) was applied to determine the concentration of magnesium and unintentional dopants. The given magnesium concentrations are accurate to within 20% deviation.

In order to support our assignment to local vibrational modes we calculated their frequencies using a model based on harmonic approximations and a modified valence-force model of Kane[9] in a cluster of 295 atoms with Mg in the center. The valence-force potentials include the bond stretching and bond bending of nearest and next-nearest neighbors, long-range interaction (bond bending between three adjacent bonds)[10] and effective-charge parameter Z* for Coulomb interactions. The anisotropy of hexagonal GaN was taken into account by introducing two sets of parameters, one describing interactions along the *c* axis and the other perpendicular to the *c* axis. To describe the change of interatomic forces in the vicinity of the defect we adopted a scaling factor approximation which assumes an equal relative change of all forces at the defect with respect to the perfect-crystal values.

Figure 1 shows Raman spectra of samples with magne-

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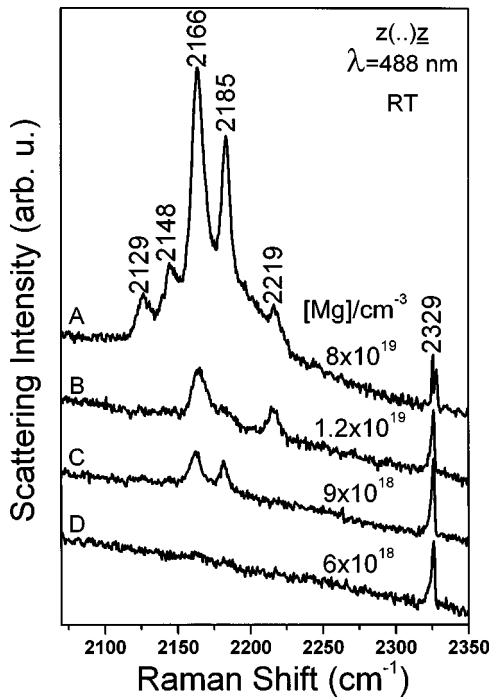
FIG. 1. Room-temperature Raman spectra of GaN with different Mg content in the high-energy range. A new mode appears at 2129 cm^{-1} for the highest Mg-doped sample.
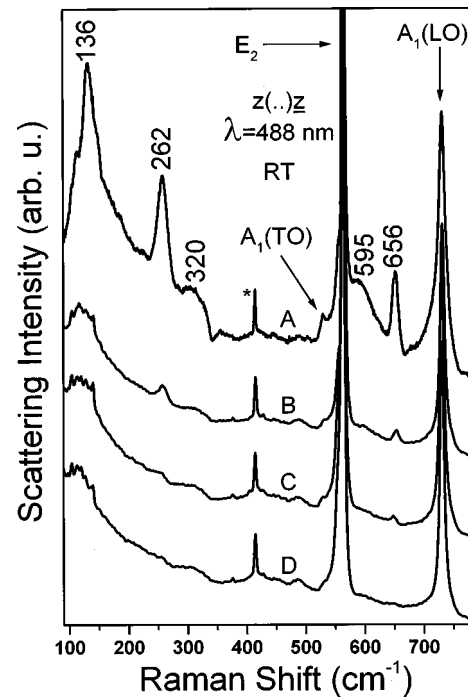

FIG. 2. Room-temperature Raman spectra (normalized to E$_2$ intensity) of GaN with different Mg content in the low-energy range. In addition to the host lattice phonons five more modes are observed. The peak marked by an asterisk is the A$_{1g}$ mode from the sapphire substrate.

sium concentrations of 8×10^{19} cm^{-3} (A), 1.2×10^{19} cm^{-3} (B), 9×10^{18} cm^{-3} (C), and 6×10^{18} cm^{-3} (D), respectively, in the high-energy region, i.e., around 2200 cm^{-1}. In the spectrum of sample A with the highest magnesium concentration a new mode appears at 2129 cm^{-1} in addition to the four local vibrational modes (LVMs) described in Ref. 4. All five modes appear in the spectrum of the highest Mg-doped sample and only a few of them in the spectra of samples B and C. In the spectrum of sample D, with a Mg-concentration of about 6×10^{18} cm^{-3}, one can recognize residual structures at 2166 and 2185 cm^{-1}. Apparently, the intensity of the modes correlates with the magnesium content. A Mg-concentration of around 1×10^{19} cm^{-3} is necessary for some of the high-energy modes to appear well-resolved in the spectra. The hydrogen concentration for all samples investigated here is in the range of 10^{19} cm^{-3} as determined by SIMS. Since hydrogen was not intentionally supplied during growth its incorporation possibly arises from the residual water vapor pressure in the growth chamber.

We believe that the origin of all five high-energy modes are Mg–H complexes with different configurations. It seems unlikely that hydrogen decorated native defects give rise to these vibrations. In particular V$_{Ga}$–H$_n$ complexes have vibrational frequencies[11] near 3100 cm^{-1} which is much higher than what we observed. We did not observe a mode at 3125 cm^{-1} which was attributed to Mg$_{Ga}$–H vibrations in GaN (MOCVD).[6] The differences in growth procedures, especially in temperature and supply of hydrogen, lead to the formation of different defect complexes related to magnesium and hydrogen in MOCVD– and MBE–GaN.

Apart for the five high-energy modes the highly Mg-doped samples exhibit new vibrational modes in the low-energy region. In this letter we refer to the region of the acoustic and optical GaN phonons from 100 to 800 cm^{-1} as

the low-energy region. We found structures at 136, 262, 320, 595, and 656 cm^{-1}. Figure 2 displays the low-energy part of the Raman spectra of the four samples in the same sequence as in Fig. 1. All these modes exhibit an A$_1$ symmetry[12] as can be seen from the polarization dependence shown in Fig. 3. The broad structures centered around 320 and 595 cm^{-1} may result from disorder-activated scattering, in which built-in defects yield a relaxation of the $q=0$ selection rule for first-
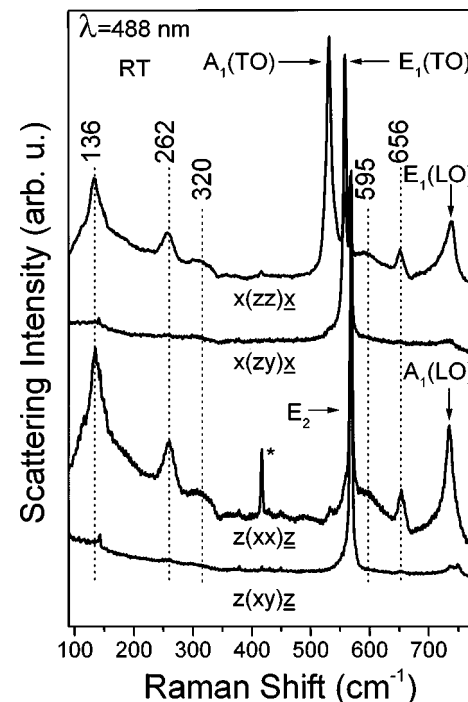

FIG. 3. Room-temperature Raman spectra of sample A for different scattering configurations indicating the A$_1$ symmetry of the new modes.

order Raman scattering and phonons from the whole Brillouin zone can be observed. This interpretation is supported by the fact that from sample D to A the forbidden A_1 transverse optical (TO) mode at 533 cm^{-1} increases considerably in intensity. Limmer *et al.*[13] reported on a disorder-activated Raman-mode around 300 cm^{-1} in ion-implanted GaN which is close to our 320 cm^{-1} mode. Furthermore, the cut-off at 340 cm^{-1} fits well with calculated phonon dispersion curves.[14,15] On the other hand, the modes at 136, 262, and 656 cm^{-1} probably do not originate from disorder-activated scattering since the phonon density of states does not exhibit marked structures in this frequency range.[15] Recently, a mode at 656 cm^{-1} was observed in GaN after annealing at 1000 °C and related to a damaged-sapphire substrate.[16] The ode we observed at 656 cm^{-1} is of different origin since it does not scale with the intensity of the sapphire mode at 418 cm^{-1} or other modes of the damaged-sapphire at, e.g., 770 cm^{-1} but rather with the Mg-concentration.

We thus believe these structures in the low-energy range to be correlated with magnesium. Equation (1) gives us a rough estimate of the magnesium local vibrational mode frequency from the effective masses of the GaN and LVM:

$$\frac{\omega_{\text{GaN}}}{\omega_{\text{LVM}}} \approx \sqrt{\frac{\mu_{\text{LVM}}}{\mu_{\text{GaN}}}}. \tag{1}$$

Assuming that magnesium occupied a gallium site we obtain a value of about 640 cm^{-1} for N–Mg vibrations using $\omega_{\text{GaN}} = \omega[E_1(\text{TO})] = 560$ cm^{-1}. To support our assignment we calculated the vibrational frequencies of a magnesium atom on a gallium site. Using the earlier described cluster with a scaling factor adjusted to $s = -0.15$, we obtained frequencies of 132, 267, and 660 cm^{-1}.[17] These results confirm the local modes of magnesium at these frequencies.

Modes with a frequency in the range of a significant phono density of states (PDOS) of the host material usually decay very fast into host–lattice vibrations and thus do not form localized states. One would expect to observe such modes only under resonant excitation conditions.[18] Exciting with different energies between 2.54 and 2.18 eV we did not observe a resonance behavior of any of the modes in question. Although the modes at 136, 262, and 656 cm^{-1} lie in the range of the acoustic and optical phonons, their observation may be possible because the PDOS is relatively low at these frequencies as confirmed by second-order Raman-scattering[14] and time-of-flight neutron spectroscopy.[15]

In order to investigate electronic Raman-scattering and a scattering mechanism similar to that known from GaN/GaAs[19,20] as the origin of the 136 and 262 cm^{-1} modes temperature-dependent measurements between 4 and 300 K were performed. No decrease in intensity with increasing temperature was observed for the low-energy modes thus excluding these scattering mechanisms. We, hence, assign the three modes in the low-energy region of Mg-doped GaN to local vibrational modes of magnesium in GaN. The Mg-concentration in the 10^{19} cm^{-3} range is apparently sufficient to observe the LVMs without resonant excitation.

In summary, Mg-doped GaN samples grown by MBE with different concentrations of magnesium were investigated. The magnesium concentration was determined by secondary ion mass spectroscopy. In the high-energy range of the Raman spectra we observed a new mode at 2129 cm^{-1} in addition to the four LVMs described in Ref. 4. All five modes scale in intensity with magnesium content. We attributed these modes to vibrations of different Mg–H complexes.

Furthermore, modes in the acoustic and optical phonon region of GaN were found at 136, 262, 320, 595, and 656 cm^{-1} which are strongly correlated with the high-energy modes and exhibit A_1 symmetry. The broad structures around 320 and 595 cm^{-1} originate from disorder-activated scattering. The other modes were assigned to local vibrational modes of magnesium in GaN. This assignment was confirmed theoretically by a cluster calculation.

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