Local vibrational modes of the Mg–H acceptor complex in GaN

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Local vibrational modes (LVMs) are reported for Mg-doped GaN grown by metalorganic chemical vapor deposition. Hetero-epitaxial layers of GaN:Mg, either as-grown, thermally activated, or deuterated, were investigated with low-temperature, Fourier-transform infrared absorption spectroscopy. The as-grown material, which was semi-insulating, exhibits a LVM at 3125 cm^{-1}. Thermal annealing increases the p-type conductivity, as established with Hall effect measurements, and proportionally reduces the intensity of this LVM. Deuteration of the activated material creates a LVM at 2321 cm^{-1}. The isotopic shift establishes the presence of hydrogen in the vibrating complex. The new LVMs are assigned to the stretch modes of the Mg–H and Mg–D complexes in GaN, with the vibrational frequencies indicative of a strong N–H bond as recently proposed from total-energy calculations. © *1996 American Institute of Physics.* [S0003-6951(96)02350-9]

The achievement of p-type electrical conductivity in Mg-doped GaN by Amano and co-workers,[1] together with the successful growth of high-quality InGaN layers, has enabled the III–V nitrides to become the materials of choice for the fabrication of light emitting diodes[2] and laser diodes[3] emitting in the visible blue/green region of the electromagnetic spectrum. Amano and co-workers[1] demonstrated that exposure of Mg-doped GaN to low energy electron beam irradiation (LEEBI) activates the acceptor dopants. It was subsequently demonstrated by Nakamura and co-workers[4] that thermal annealing near 800 °C in a hydrogen-free ambient also produces p-type conductivity. These postgrowth treatments are necessary because as-grown, Mg-doped GaN is semi-insulating when grown by techniques that furnish a hydrogen-rich ambient such as metalorganic chemical vapor deposition (MOCVD). In the growth of GaN with MOCVD, hydrogen is present as a carrier gas and in the nitrogen precursor, NH_3, as well as in the metalorganics themselves. In contrast, when grown by molecular beam epitaxy in the absence of hydrogen, Mg-doped GaN exhibits p-type conductivity in the as-grown state.[5]

Nakamura and co-workers[4] suggested that electrically inactive acceptor-hydrogen complexes form after growth by MOCVD which are responsible for the semi-insulating nature of the material. They observed that thermal annealing of specimens of LEEBI-treated, p-type GaN:Mg at temperatures above 600 °C in an NH_3 atmosphere decreased the conductivity by six orders of magnitude, whereas a similar anneal in a N_2 ambient left the conductivity unchanged.

From first-principles total-energy calculations, Neugebauer and Van de Walle[6] have found that isolated hydrogen should be an interstitial donor in GaN:Mg under MOCVD growth conditions and is, therefore, able to compensate deliberately incorporated Mg acceptors. They have also found that hydrogen can form a stable complex with Mg, to be further discussed below. However, all of the experimental evidence for the existence of the Mg–H complex reported to date have been indirect. The issue as to whether at room temperature the high resistivity of as-grown GaN:Mg arises from compensation or hydrogen passivation remains unresolved.

In this study, we present direct spectroscopic evidence that hydrogen forms a complex with the shallow acceptors (Mg_{Ga}) in Mg-doped GaN and that the activation process is due to the dissociation of these Mg–H complexes. We observed both H- and D-related local vibrational modes (LVMs) in as-grown and deuterated samples, respectively. Further, upon activation of the p-type conductivity, the intensities of the H- and D-related LVMs were found to decrease in inverse proportion to the increase in the conductivity. The LVMs were observed only in Mg-doped GaN and are absent in infrared absorption spectra of undoped and Si-doped GaN.

A previous study reported two LVMs (with room-temperature frequencies of 2168 and 2219 cm^{-1}) in Mg-doped GaN grown by molecular beam epitaxy that were tentatively assigned to inequivalent configurations of hypothetical Mg–H complexes in the wurtzite lattice.[7] However, neither the effect of isotopic substitution nor correlations with activation/deactivation of the p-type conductivity was presented in that study, and it was suggested that the observed modes might alternatively arise from a H-decorated native defect, such as a nitrogen vacancy with one or more of the Ga dangling orbitals passivated by hydrogen.

The GaN epitaxial layers utilized in this study were grown by MOCVD and doped with Mg during growth. The films were 4 μm thick and deposited on double-polished sapphire substrates. The concentration of Mg atoms incorporated was determined with secondary ion mass spectrometry (SIMS) to be $\sim 5\times 10^{19}$ cm^{-3}. To achieve p-type conductivity, the Mg-doped GaN samples received a standard post-growth thermal treatment in a rapid-thermal-anneal (RTA)

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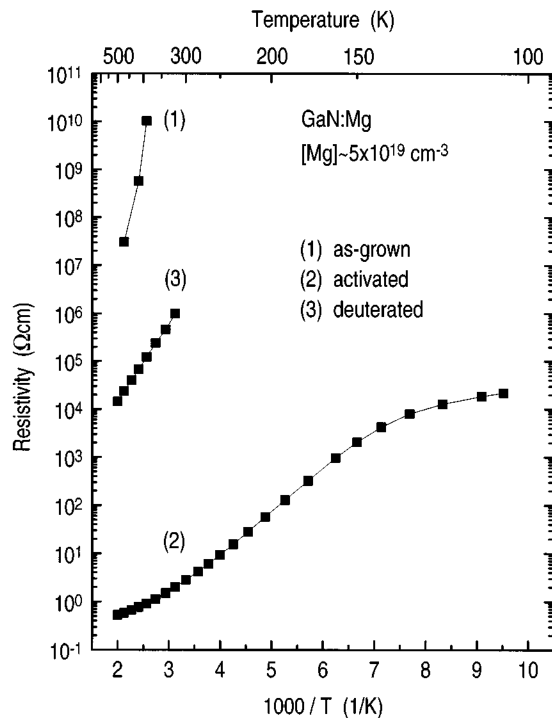

FIG. 1. Electrical resistivity vs reciprocal temperature for Mg-doped GaN: (1) for as-grown material, (2) after thermal activation of the p-type conductivity, and (3) after exposure to monatomic deuterium in a remote plasma system at 600 °C.

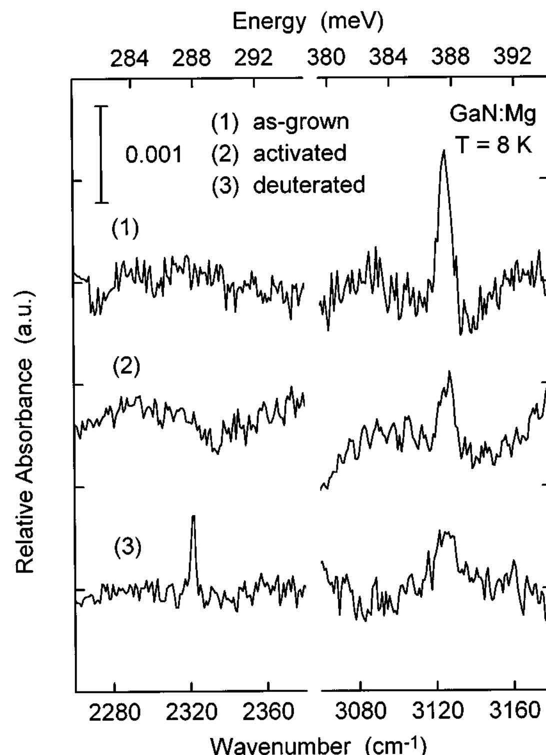

FIG. 2. Infrared absorption spectra for Mg-doped GaN grown by MOCVD. Spectra are shown for as-grown material (1), after RTA activation of the p-type conductivity (2), and after deuteration (3). The vertical bar indicates the magnitude of the absorbance scale.

system.[8] After activation, the total acceptor concentration was $\sim 2\times 10^{19}$ cm^{-3} as determined from variable temperature Hall effect measurements.[9] The hole mobility was ~16 cm^2/V s at 300 K, with a maximum of ~27 cm^2/V s at 190 K. Deuteration was performed with a remote plasma hydrogenation system[10] at 600 °C for two hours. Such a treatment introduces deuterium into the p-type, Mg-doped GaN at concentrations above 10^{19} cm^{-3} and significantly increases the resistivity of the films.[10]

Infrared absorption measurements were performed with a Fourier-transform infrared (FTIR) spectrometer (Bomem DA8) equipped with a mercury cadmium telluride (MCT) detector and a glowbar light source. We used a CaF_2 and KBr beam splitter for the H- and D-related peaks, respectively. An instrumental resolution of 2 cm^{-1} was sufficient to fully resolve the peaks. The samples were placed in a Janis liquid-helium dewar and kept at a temperature of 8 K. The doped GaN samples and the references were placed on the same mounting plate to ensure accurate and reliable subtraction of the background. The absorption measurements were performed in transmission at normal incidence.

The electronic properties of Mg-doped GaN after the various treatments are illustrated in Fig. 1 for devices optimized for Hall measurements on material similar to that used for the FTIR measurements. The resistivity is shown as a function of temperature for the as-grown material (1), after activation of the p-type conductivity (2), and after deuteration at 600 °C (3). The as-grown material is essentially semi-insulating with the resistivity approaching $\sim 10^{10}$ Ω cm at 400 K. After RTA treatment, the resistivity decreases to ~2 Ω cm at 300 K, due to activation of the acceptors. The deuteration increases the resistivity of the film to $\sim 10^{6}$ Ω cm at room temperature.

Figure 2 presents infrared absorption spectra for the Mg-doped GaN. The relative absorbance [$\equiv -\ln(\mathcal{T}/\mathcal{T}_0)$, where $\mathcal{T}/\mathcal{T}_0 \equiv$ transmittance with/without the sample] is shown in two different wavenumber ranges. For the as-growth material (1), the spectrum exhibits a LVM line at 3125 cm^{-1}. After thermal activation (2) of the acceptors, the intensity of this line is reduced by about a factor of two. After deuteration (3), a new absorption line appears at 2321 cm^{-1}. This line disappears after the thermal activation treatment (not shown in Fig. 2).

Our experimental data clearly indicate that the LVM with the frequency of 3125 cm^{-1} (Fig. 2) is a vibrational mode of the Mg_{Ga}-H complex in GaN. First, this mode appears only in Mg-doped GaN and, second, an isotopic shift of the vibrational frequency is clearly established with the absorption line at 2321 cm^{-1} (Fig. 2) which appears in deuterated samples. The isotopic ratio of the two absorption line frequencies is ~1.346, close to $\sqrt{2}$ and in excellent agreement with the corresponding frequency ratios observed for H-related LVMs in other semiconductors (e.g., Refs. 11 and 12).

Further evidence for a Mg–H complex is provided by the correlation of the intensity of the LVM absorption lines with the p-type conductivity of Mg-doped GaN films. The intensity of the absorption line at 3125 cm^{-1} decreases significantly upon activation of the p-type dopant. This observation is consistent with the model that after growth most of the Mg acceptors are passivated by hydrogen. The Mg–H

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complexes are electrically inactive and give rise to the LVM line observed by FTIR spectroscopy. In the as-grown material, only a small fraction of the Mg atoms is required to act as acceptors to compensate the residual donors.[6] As a consequence, as-grown Mg-doped GaN is highly resistive. Under the assumption that practically all of the Mg atoms (5×10^{19} cm^{-3}) in the as-grown material form complexes with hydrogen, the optical cross section for the observed absorption line is estimated to be $\sim 10^{-19}$ cm^2. This should be considered only an order-of-magnitude estimate since the SIMS data are accurate to only 50% and our measurement geometry excluded Mg–H complexes aligned parallel to the c-axis of the GaN crystal (as further discussed below).

The postgrowth activation treatment results in the dissociation of the Mg–H complexes. As a consequence, the intensity of the LVM line at 3125 cm^{-1} decreases (Fig. 2). From the intensity ratio of the LVM line in the as-grown and the annealed samples, we estimate that $\sim 3 \times 10^{19}$ cm^{-3} of the Mg acceptors became activated. This number is in good agreement with the concentration of acceptors in the activated film as determined from the variable temperature Hall measurements (2×10^{19} cm^{-3}). It has been shown that isolated hydrogen acts as a donor in p-type GaN and is highly mobile.[6,9] During the activation process, the hydrogen atoms are likely either to evolve out of the sample or are immobilized at internal sites where they cease to influence the p-type conductivity.

Our assignment for the stretch mode of the Mg–H complex in GaN is consistent with recent computational studies.[6] These studies, which utilized first-principles total-energy calculations based on density-functional theory and *ab initio* pseudopotentials, suggested a novel atomic structure which is qualitatively different from the bond-centered-hydrogen configuration that has been well established for acceptor-hydrogen complexes in other semiconductors. The hydrogen atom prefers the antibonding site of one of the N neighbors of the substitutional Mg. Thus, the Mg–H complex contains a N–H bond with a calculated H-stretch mode frequency of 3360 cm $^{-1}$, very close to that of H in NH_3 (3444 cm^{-1}). Infrared absorption spectra of N–H complexes in ZnSe[13,14] show a single strong LVM line at 3195 cm^{-1}, very close to the stretch vibration of the Mg–H complex reported here and again consistent with ammonia-moleculelike hydrogen stretch vibrations.

In wurtzite GaN, one might expect two distinct stretch vibrational modes of the Mg–H complex due to the two inequivalent sites. Specifically, the axis of the complex can be aligned either parallel (i.e., IR dipole parallel to the c-axis) or perpendicular to the c axis (i.e., IR dipole perpendicular to the c axis). Since in the present study only illumination normal to the sample surface (i.e., parallel to the c axis) was possible, we were sensitive only to complexes in the c plane and cannot rule out the existence of a second LVM line from c-axis aligned complexes. However, because the deviation of the GaN wurtzite structure from the perfect diamond structure is rather small, we expected the differences in the N–H stretch vibrational frequencies of Mg–H complexes parallel and perpendicular to the c axis also to be rather small, perhaps too small to be resolved.

In summary, we have established spectroscopically that Mg acceptors are passivated by hydrogen in as-grown GaN films grown by MOCVD. The high frequency of the observed LVM is compatible only with a stretch vibration of H bound to N. The observed isotopic shift unambiguously establishes the presence of H in the complex. Our observations are consistent with a theoretically proposed model for the Mg–H complex which places the H in an antibonding position bound to a N neighboring the Mg_{Ga} acceptor.

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