

Infrared spectroscopy of Mg-H local vibrational mode in GaN with polarized light

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Magnesium-doped GaN grown by organometallic vapor phase epitaxy has been investigated by multitransmission infrared spectroscopy with the wave vector not along the c axis. This allows searching for local vibrational modes of complexes aligned along the c axis that cannot be seen by “normal” optical configuration. This technique, combined with polarized light, allows the precise determination of the geometry of the complexes. It has been found that the stable “magnesium-hydrogen” complex is not aligned along the c axis. The structure of this complex, including the angle between the electric dipole induced by the local mode and the c axis, has been determined. No other hydrogen-related complex aligned along the c axis has been detected.

I. INTRODUCTION

The role of hydrogen in the most common III-V semiconductors is relatively well understood.^{1,2} It neutralizes acceptors and, at least in GaAs and GaP, donors; it can also passivate lattice defects. The structure of the resulting complexes has been determined.^{1,2} It is also well known that hydrogen can be present unintentionally in these materials being introduced either during the growth or processing.¹⁻³

GaN is a material which is presently widely investigated because of its potential use in short wavelength solid-state LASER technology. Organometallic vapor phase epitaxy (OMVPE) is the most common growth technique of GaN and there are evidences that hydrogen coming from the organometallic precursors might neutralize the acceptors in this material as well, leading to a very weak electrical activity in as-grown GaN doped with acceptors.⁴ It has also been proposed that hydrogen could help in the doping of GaN.^{5,6} As a consequence, there is a great interest for hydrogen in GaN at the moment. Theoretical investigations have shown that, because of the great electronegativity of nitrogen, hydrogen should behave differently in GaN and in the “usual” III-V compounds GaAs, GaP, and InP.⁷⁻⁹ Some of the theoretical predictions have still not been confirmed experimentally; in particular, it has not been proved whether, in the “acceptor-hydrogen” complexes, hydrogen sits in antibonding position, as predicted by theory,⁷⁻⁹ or in bond center location.¹⁰

Vibrational spectroscopy is a very powerful technique in the investigation of hydrogen in the conventional III-V semiconductors.^{2,11} As a matter of fact, there are only few reports¹²⁻¹⁴ on the spectroscopic investigation of the neutralization of acceptors in GaN; in particular a local mode of vibration related with the complex resulting from the neutralization of magnesium by hydrogen has been observed at 3125 cm^{-1} in as grown OMVPE GaN.¹³ The reason for this

small amount of data comes from the fact that the available samples are most often epilayers. Spectroscopic experiments on such samples are not easy for several reasons: (i) the thickness of the layer is rather small ($\approx 1\ \mu\text{m}$), (ii) the large lattice mismatch between the substrate (most often sapphire) and the GaN layer induces strains in the layer, which broaden the local vibrational modes, (iii) the substrates are most often opaque in some spectral regions of interest, and (iv) the “usual” experimental configuration might forbid the observation of some types of complexes. This last point comes from the fact that the GaN layers have most often the wurtzite structure (thermodynamically stable) with the c -axis perpendicular to the layer; as the vibrational transitions are dipolar-electric allowed, the stretching mode of a complex aligned along the c axis cannot be detected in “usual” experiments in which the light beam is perpendicular to the sample. In order to overcome the (ii) and (iii) difficulties, it is necessary to change the sample elaboration conditions and in particular the substrate; on the other hand, one can improve (i) and overcome (iv) by a proper choice of the spectroscopic experimental conditions.

In this paper, it will be reported on the investigation of magnesium-doped OMVPE-grown GaN layers by multitransmission experiments. This type of experiment allows on the one hand to increase the optical path length within the layer and on the other hand to perform experiments with nonequivalent polarizations of the light and thus to search for stretching modes of vibration of a complex aligned perpendicularly to the layer.

II. EXPERIMENTS

The optical absorption experiments have been performed using BOMEM DA3+ and DA8 Fourier transform interferometers equipped with calcium fluoride beam splitters and indium antimonide cooled detectors. The experiments are

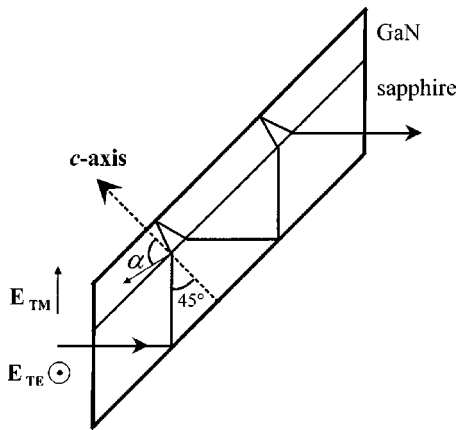


FIG. 1. Principle of the multitransmission spectroscopy. In the TE polarization, the electric field is perpendicular to the c -axis whereas in the TM polarization, it makes an angle α with the c axis in the epilayer.

performed at temperatures around 5 K using Oxford Instruments CF 204 or CF 1204 cryostats.

The principle of the multitransmission setup is represented in Fig. 1. The incidence angle with respect to the sample large surfaces is $\pi/4$. Due to the high refraction indexes of both the substrate and the layer, one obtains total reflections on the sample large surfaces, but no total reflections at the interface between the substrate and the layer. This technique needs the sample to have two parallel polished side faces making a $\pi/4$ angle with respect to the main faces. Figure 2 gives a scheme of the setup which is inserted inside of the cryostats. Mirror $M2$ is fixed on the setup whereas mirror $M1$ is adjustable as a function of the sample length. The adjustment of mirror $M1$ is made at room temperature outside of the cryostat using a visible laser. The

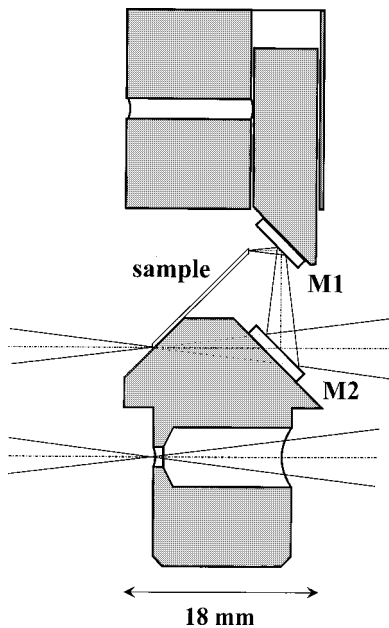


FIG. 2. Scheme of the optics inserted inside of the cryostat. The mirror $M1$ can be adjusted depending on the sample length by translating the cylinder on which it is fixed. A vertical translation of the whole insert allows both to make a reference spectrum and a spectrum through the sample.

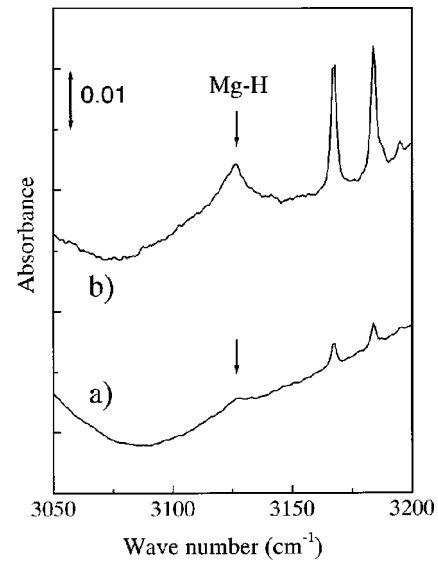


FIG. 3. Absorbance of a magnesium-doped GaN sample grown by OMVPE measured (a) with conventional transmission spectroscopy, (b) with multitransmission spectroscopy. The line at 3125 cm^{-1} is due to the complex resulting from the neutralization of magnesium by hydrogen in the GaN layer whereas the sharper lines at higher wave numbers are due to the sapphire substrate.

beam of the interferometer is focused on the entrance side face of the sample. After reflections on the mirrors $M1$ and $M2$, the optical axis of the beam is the same as the optical axis of the incident beam on the sample. Because of the small thickness of the sample, vertically, the exit side face of the sample is practically also a focus of the beam. Therefore, in the plane of Fig. 2, the geometry of the beam after reflection on mirror $M2$ is practically the same as the one of the reference beam and it does not depend upon the sample length. However, in the direction perpendicular to Fig. 2 the sample has introduced a defocusing, i.e., the section of the beam is no longer circular after having passed through the sample. The sensitive area of the detector being larger than the image of the iris, this does not introduce any significant loss of light.

The magnesium-doped GaN layers investigated have been grown by OMVPE at about 1000°C on sapphire substrates. They are of wurtzite structure with the c axis perpendicular to the layer. Mg acceptor concentration exceeds 10^{19} cm^{-3} . As grown samples are insulating at room temperature.

III. RESULTS WITH NATURAL LIGHT

Figure 3 shows part of the infrared spectrum of a magnesium-doped as-grown sample recorded both with “normal” configuration [trace (a)] and “multitransmission” configuration [trace (b)]; the length of the sample is 5 mm and its thickness (substrate+layer) 1 mm. The 3125 cm^{-1} broad signal is due to the complex resulting from the neutralization of the magnesium acceptor by hydrogen in GaN (Ref. 13) whereas the lines at higher energies are due to the substrate. As expected, all the lines are about 6 times more intense in trace (b) than in trace (a) because of the increase in optical pass through the whole sample.

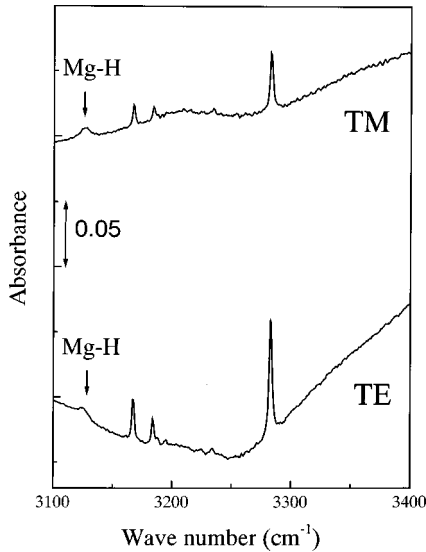


FIG. 4. Absorbance of the same sample as in Fig. 3 with TM and TE polarizations. As in Fig. 3, the line at 3125 cm^{-1} corresponds to the “magnesium-hydrogen” complex and the sharper lines are due to the sapphire substrate.

It has to be noted that we could not detect any additional mode by use of the “multitransmission” configuration with respect to measurements in “normal” configuration. In particular, we did not detect the modes around 2200 cm^{-1} observed by Raman and infrared spectroscopies in magnesium-doped GaN grown by molecular-beam epitaxy.^{12,14}

After annealing of the as grown samples at 800°C in nitrogen ambient, the mode at 3125 cm^{-1} is no longer observable and at the same time, the samples become *p*-type conducting. Holes concentrations at room temperature up to $6 \times 10^{17}\text{ cm}^{-3}$ have been obtained in our experiments after Mg activation caused by the annealing.

IV. INVESTIGATION WITH POLARIZED LIGHT

Experiments have been performed with the two TE and TM polarizations indicated in Fig. 1. With the TE polarization, the electric field of the light is perpendicular to the *c* axis whereas with the TM polarization, the electric field inside the sample has both a component parallel to the *c* axis and one perpendicular to it. In the TM configuration, the electric field inside of the GaN epilayer makes an angle α with the *c* axis; the angle α depends upon the refraction indexes of both the substrate and the epilayer.

Figure 4 shows the absorption spectra of the same sample as the one used for Fig. 3 with the TE and TM polarizations. The broadest line at 3125 cm^{-1} is due to “magnesium-hydrogen” complex in the epilayer whereas all the lines at higher energy are due to O-H related complexes in the sapphire substrate. It has to be noted that all the lines observed with the TM polarization are also seen with the TE polarization. This confirms that none of the modes observed corresponds to a complex aligned along the *c* axis of the epilayer or of the substrate. However, one notices a clear dependence of the intensity of the lines with the polarization. For instance for the 3282 cm^{-1} substrate mode: $I_{\text{TE}}/I_{\text{TM}} = 2 \pm 0.1$ and for the “magnesium-hydrogen” complex in GaN at 3125 cm^{-1} : $I_{\text{TE}}/I_{\text{TM}} = 0.9 \pm 0.1$.

V. ANALYSIS OF THE EXPERIMENTS WITH POLARIZED LIGHT

A priori, there were two possible types of complexes resulting from the neutralization of magnesium by hydrogen: the first one (type I) in which the complex is aligned along the *c* axis and the second one (type II) in which the electric dipole induced by the vibration makes an angle θ with the *c* axis; because of the symmetry of the crystal, there are three equivalent configurations for type-II complexes. The experiments reported in Secs. III and IV show that no type-I complex is observed neither in the GaN layer nor in the substrate.

As the birefringence of both GaN and sapphire is small (around 1% or smaller), it has been neglected for analyzing quantitatively the results obtained in the previous section. The intensity of the light absorbed by a type-II mode can be written

$$I \propto \sum_{i=1}^3 \cos^2(\mathbf{E}, \mathbf{p}_i),$$

where the summation is over the three equivalent configurations, \mathbf{E} is the electric field of the light and \mathbf{p}_i is the electric dipole induced by the vibration of a complex in the configuration *i*. Straightforward calculations show that:

$$\frac{I_{\text{TE}}}{I_{\text{TM}}} = \frac{\sin^2 \theta}{(3 \cos^2 \alpha - 1) \cos^2 \theta + \sin^2 \alpha}. \quad (1)$$

In order to check the validity of our experiments, one can analyze the substrate line at 3282 cm^{-1} . This line is due to a stretching mode of a complex involving unintentional hydrogen in which the oxygen-hydrogen bond lays and vibrates in a plane perpendicular to the *c* axis of sapphire;¹⁵ therefore, for this mode $\theta = \pi/2$. In the substrate, $\alpha = \pi/4$. Therefore, Eq. (1) predicts $I_{\text{TE}}/I_{\text{TM}} = 2$ in perfect agreement with the experimental result described in Sec. IV.

In the GaN layer, α is given by the refraction laws. Using 1.7 for sapphire and 2.3 for GaN as refraction indexes at 3125 cm^{-1} , one obtains $\alpha = 58.5^\circ$. Using the 0.9 ± 0.1 ratio determined in Sec. IV, one deduces from Eq. (1) that for the complex responsible for the 3125 cm^{-1} mode one has $\theta = 130 \pm 5^\circ$. This angle is the angle between the *c* axis of the crystal and the electric dipole induced by the mode. Hydrogen must have the largest amplitude in the 3125 cm^{-1} stretching mode; therefore, θ should not be very different from the angle between the N-H bond and the *c* axis. The structure of the complex resulting from the neutralization of the magnesium acceptor by hydrogen is schematized in Fig. 5. It has a C_s (C_{1h}) symmetry, the mirror plane being the plane formed by the N-H axis and the *c* axis. In Fig. 5, hydrogen has been located in antibonding position. This cannot be deduced from the experiments described in this paper. The antibonding location of H atom proposed by theory⁷⁻⁹ has been adopted in Fig. 5.

VI. DISCUSSION AND CONCLUSION

It has been shown that the stable complex resulting from the neutralization of the magnesium acceptor in GaN is of type II, i.e., in a configuration having C_s (C_{1h}) symmetry as schematized in Fig. 5. This result is in agreement with the

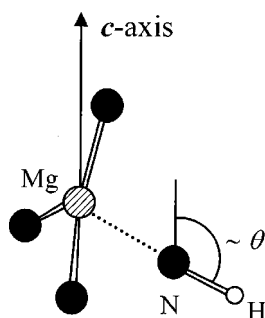


FIG. 5. Schematic representation of the stable complex resulting from the neutralization of magnesium by hydrogen in GaN.

theoretical prediction of Bosin, Fiorentini, and Vanderbilt.⁸ The angle between the electric dipole induced by the local mode and the c axis has been determined experimentally to be $\theta = 130 \pm 5^\circ$.

This result can be related with those obtained by perturbed $\gamma\gamma$ angular correlation spectroscopy on the “cadmium-hydrogen” complex in GaN.^{16,17} In these works, the complexes were created by implantation. Proton implantation at 50°C leads to the creation of both type-I and type-II complexes.^{16,17} Their thermal stability has been investigated¹⁷ and the type-I complexes dissociate at 370 K whereas the type-II ones are stable until around 600 K. If the proton implantation is performed at 100°C , only type-II complexes are observed.¹⁸ In the case of the samples investigated in this paper, the “magnesium-hydrogen” complexes

are formed during the cooling down of the samples; the complexes can only be formed at a temperature sufficient for the precursors to pyrolyze, but lower than the complex dissociation temperature.³ If the type-I “magnesium-hydrogen” complexes are less stable than the type-II ones, as it is the case for “cadmium-hydrogen” complexes, it is quite likely that the formation condition is fulfilled only for the type-II complexes. It would be of interest to create “magnesium-hydrogen” complexes by proton implantation at low temperature of equilibrium doped GaN in order to see whether in such out of equilibrium condition type-I complexes could be observed as well.

According to theory,⁷⁻⁹ hydrogen sits in anti-bonding location close to a nitrogen atom in the “magnesium-hydrogen” complex as represented in Fig. 5. In such circumstance, transverse modes of the complex are expected to exist at relatively high wave number (of the order of 1000 cm^{-1}). Unfortunately such modes could not be observed because of the non-transparency of the sapphire substrate in this spectral range. Experiments with samples grown on substrates transparent in this spectral range, for instance homoepitaxial layers grown on bulk GaN, would be most interesting for confirming experimentally the antibonding location of hydrogen in the complex.

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