PHYSICAL REVIEW B VOLUME 58, NUMBER 20 15 NOVEMBER 1998-II

Raman scattering from defects in GaN: The question of vibrational or electronic scattering mechanism

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(Received 16 July 1998)

We present a comprehensive Raman study on defects in GaN, which appear in the Raman spectra as sharp and intense lines in the low-energy region from 95 to 250 cm^{-1}. These lines decrease nearly exponentially in intensity with increasing temperature and are excitable only in the range 2.0–2.5 eV. Their temperature behavior seems to be incompatible with vibronic excitations but indicates an electronic-scattering mechanism. However, our magnetic-field- and high-pressure-dependent Raman measurements contradict this interpretation. We show in contrast that all lines are caused by vibrational Raman scattering in which the temperature dependence is due to the resonance process. We demonstrate in a doping study that the responsible defects are related to As impurities incorporated into the GaN material. [S0163-1829(98)00344-0]

I. INTRODUCTION

Low-temperature Raman spectra of GaN films grown epitaxially on GaAs, apart from the host lattice modes, show a series of sharp lines in the low-energy spectral region. The intensity of these lines decreases nearly exponentially with increasing temperature and the lines disappear at room temperature. Since a vibrational Raman-scattering process should exhibit the opposite temperature behavior, i.e., an increase with increasing temperature,[1] an electronic origin of these Raman lines seemed to be very likely. Ramsteiner *et al.* reported on the observation of four such lines and interpreted these as electronic Raman transitions in a shallow donor in GaN.[2] However, our measurements reveal the occurrence of additional lines which do not fit this model.[3] In contrast, we present in this work evidence that all lines are of vibrational, and not of electronic, origin and we show that the responsible defects are related to the incorporation of As impurities into the GaN layers.

We performed a comprehensive Raman study on several series of doped and undoped GaN films deposited on GaAs as well as on sapphire substrates. Magnetic-field- and high-pressure-dependent Raman measurements on our samples allowed us to ascertain the scattering mechanism. Our results indicate that these lines are resonant (band) modes caused by defects in the GaN layer. In order to identify the responsible defects we compared several series of GaN layers grown on different substrates and by different methods. Only those films deposited on GaAs exhibited the additional Raman lines. We thus assumed that the incorporation of As during the growth of the GaN epilayers on the GaAs substrates leads to the formation of the responsible defects. In order to prove our assumptions we performed measurements on GaN films that were grown on sapphire but that were intentionally doped with As.

The additional Raman lines can be excited only in the yellow to green spectral region. Thus their excitation profiles are in the same spectral region where the yellow luminescence of GaN is located, and a direct link seemed to be likely.[2] However, pressure-dependent measurements presented in this work show that there is no direct connection.

After presenting the experimental techniques in Sec. II, we give a brief description of the temperature and the resonance behavior of the lines in question (Sec. III A). In Secs. III B and III C we present the results of our magnetic-field-dependent and hydrostatic-pressure-dependent measurements. We then turn to the identification of the responsible defects comparing spectra taken from doped and undoped GaN films grown on GaAs and on sapphire (Sec. III D). In Sec. IV we summarize all effects and draw a model of the scattering process.

II. EXPERIMENT

The samples under study were several series of GaN layers grown on (001) GaAs by molecular-beam epitaxy (MBE) and on (0001) sapphire by metal-organic chemical vapor deposition (MOCVD), hydride vapor phase epitaxy (HVPE), and MBE. Thicknesses vary between 0.5 and 2 μm in the case of the MBE samples and up to 400 μm in the case of the HVPE samples.

The Raman-scattering experiments at ambient conditions were carried out in backscattering geometry with a triple-grating spectrometer equipped with a cooled charge-coupled device (CCD) detector. An $\mathrm{Ar}^+/\mathrm{Kr}^+$ mixed-gas laser was used for excitation in the range 458–676 nm. Parts of the experiments were performed with a microscope setup with a spatial resolution better than 1 μm. The sample temperature was varied in the range 2–300 K using either an Oxford microscope cryostat in the case of micro-Raman measurements or an Oxford bath cryostat.

The high-pressure Raman experiments were performed in a gasketed diamond-anvil cell at low temperatures (10 K) using liquid helium as the pressure-transmitting medium. The shift of the *R*-line luminescence was used to calibrate the pressure inside the cell.[4] Prior to the experiment, the sub-

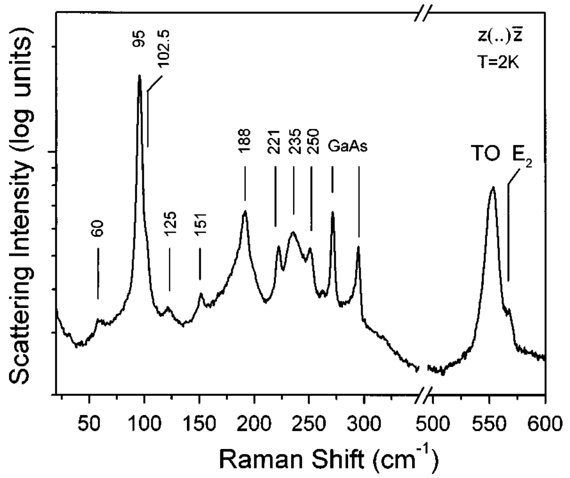

FIG. 1. Overview of the defect modes in GaN grown on GaAs. The spectrum was taken in $z(\ldots)\bar{z}$ configuration at 2 K with excitation at 514.5 nm (2.41 eV).

strates of the samples were mechanically thinned. Finally, the samples were cleaved and placed in the gasket hole of the diamond-anvil cell. The 488-, 502-, and 514.5-nm lines of an Ar^+-ion laser were used for excitation. As in the experiments at ambient conditions the scattered light was detected in backscattering geometry corresponding to $z(\ldots)\bar{z}$ and analyzed by means of a triple-grating spectrometer equipped with a CCD.

III. RESULTS

Figure 1 gives an overview of the lines investigated in this work. It shows a typical low-temperature Raman spectrum of a GaN layer grown on GaAs excited at 514.5 nm (2.41 eV). Apart from the host phonon modes of GaN [cubic TO and hexagonal E_2 (high)] and GaAs (TO and LO) the low-energy part of the spectrum consists of several sharp lines, which are even more intense than the host Raman modes. We found in total at least 10 of these lines. The most intense lines are located at 95, 150, 190, 220, 235, and 250 cm^{-1}.

At first glance, considering the energy positions, one might want to assign these lines to second-order Raman scattering or to disorder-activated scattering either in the GaN layer or in the substrate. But the comparison with second-order Raman spectra of cubic and hexagonal GaN (Ref. 5) as well as of GaAs (Ref. 6) and the consideration of the phonon dispersions[5] show that these low-energy lines cannot stem from the GaN or GaAs host lattices. The low-energy parts of the second-order Raman spectra of GaN are dominated by structures at 314 and 415 cm^{-1}. The lowest flat-running phonon branches that lead to a high phonon density of states and thus should be seen in disorder-activated scattering are located at approximately 150 cm^{-1}. Consequently, the lines in question can only stem from defects built into the host material. These defects become visible in the Raman spectra either due to their vibronic or electronic excitations. For reasons of readability we will call these lines, in the following, defect lines. To scrutinize that they are related to the GaN layer and not to the substrate, we also performed spatially resolved micro-Raman measurements as well as measurements on series of samples with varying thicknesses. Both measurements confirm that the lines occur only in the GaN films. Figure 2 shows such a linescan over the cross section of a GaN/GaAs interface. One can clearly see that the intensities of the defect lines follow that of the GaN TO phonon mode, verifying that they stem from the GaN layer and not from the substrate. We will now focus on the question of the scattering mechanism (Secs. III A–III C) and then turn to the

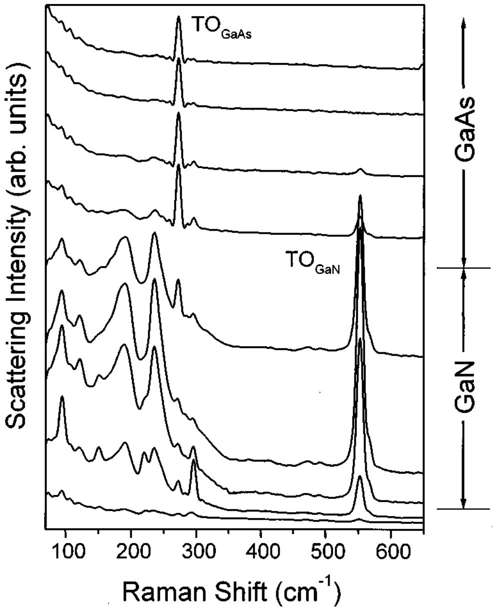

FIG. 2. Linescan in $x'(\ldots)\bar{x}'$configuration with $x' = [110]$ across a GaN/GaAs sample in which every 0.5 μm one spectrum was taken. The temperature was 4.2 K, the excitation was at 514.5 nm (2.41 eV). One can clearly see that the defect lines occur only in the GaN layer.

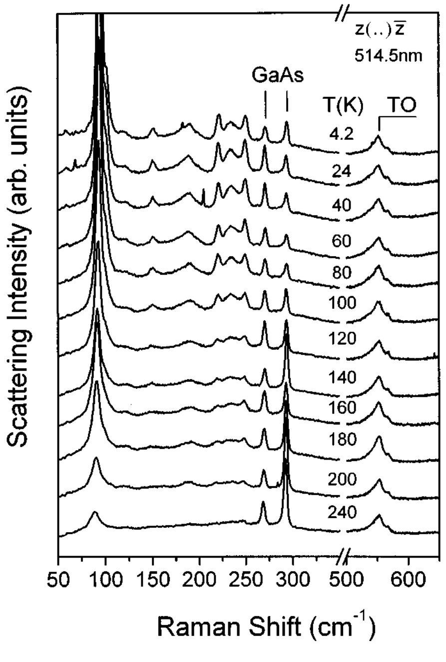

FIG. 3. Series of Raman spectra taken from a GaN/GaAs sample at different temperatures. The excitation wavelength was 514.5 nm (2.41 eV). All spectra are Bose corrected and normalized to the intensity of the GaN TO mode. The intensity of the defect lines decreases nearly exponentially with increasing temperature.

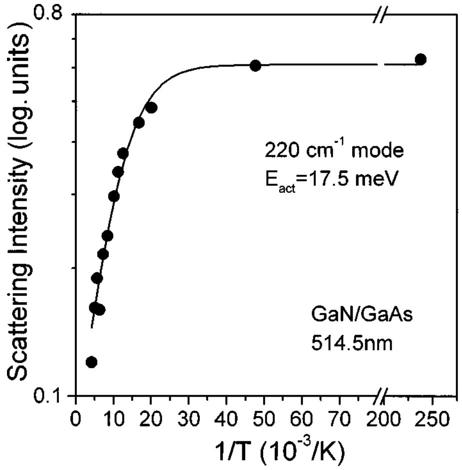

FIG. 4. Arrhenius plot of the temperature dependence of the 220-cm^{-1} defect mode in GaN/GaAs.

identification of the defects involved in the scattering process.

A. Temperature and resonance behavior

Figure 3 displays the remarkable development of the Raman spectrum of Fig. 1 with increasing temperature: In contrast to the GaN and GaAs host phonon modes the defect lines weaken and nearly disappear at 240 K. The intensity variation with temperature $I(T)$ may be fitted by the expression[2]

$$I(T)=\frac{A}{1+C\exp\left(-\frac{E_{\mathrm{act}}}{kT}\right)},\qquad (1)$$

as shown in the Arrhenius plot in Fig. 4, which gives us an activation energy E_{act} of each line. The parameters A and C are temperature independent. We found activation energies in the range 10–60 meV depending on line and sample.

The temperature behavior confirms the exclusion of host-lattice vibrations. In general, Raman scattering from lattice vibrations is supposed to show an increasing signal with increasing temperature.[1] The defect lines exhibit the opposite behavior, they decrease with temperature and vanish at room temperature. However, vibrational Raman scattering from built-in defects should not exhibit the observed temperature behavior. One might conclude that the defect lines are caused by electronic excitations of the defects in which the thermal occupation of the involved electronic states leads to the peculiar temperature dependence.

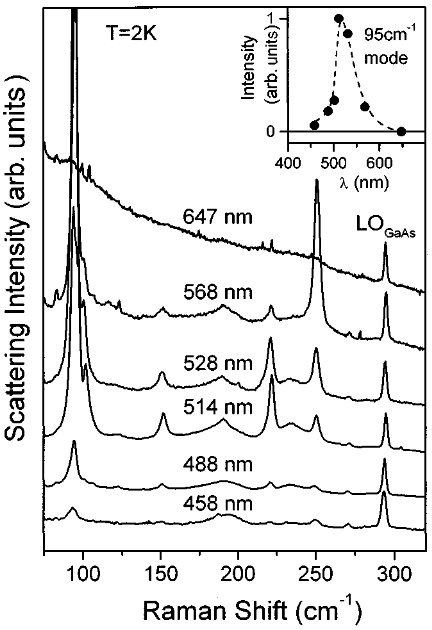

FIG. 5. Low-temperature Raman spectra taken in $z(\ldots)\bar{z}$ configuration with different excitation wavelengths between 458 nm (2.71 eV) and 647 nm (1.92 eV) demonstrating the strong resonant behavior of the defect lines. The inset shows the resonance profile of the 95-cm^{-1} defect mode. The measured intensities for every excitation wavelength were normalized to the scattering intensity of the $\mathrm{BaF_2}$ mode. Except the mode at 250 cm^{-1} all defect lines exhibit a similar excitation behavior.

To answer this question one has to consider first which vibronic excitations of defects are possible. One distinguishes between local modes, gap modes, and resonant (band) modes.[7,8] If the impurities built into the host lattice are of lower mass than the host atoms one can observe local modes with frequencies higher than the phonon dispersion of the host lattice. This is obviously not the case here. Also, gap modes may be ruled out. The defect lines are located in the acoustic region of the GaN phonon dispersion where no gap in the phonon density of states exists.[5] In principal, those defect modes, which are degenerate with acoustic vibrations of the host material, cannot be observed because motion relevant to the defect will rapidly degenerate into motion of the surrounding lattice, providing no discrete phonon states. Those modes can only be excited under resonant conditions [resonant (band) modes]. Indeed, our defect lines exhibit a strong resonance behavior. They are excitable only in the region of the yellow luminescence between 2.0 and 2.5 eV, as can be seen from the Raman spectra taken with different excitation energies displayed in Fig. 5. It is thus conceivable that the lines are caused by vibronic excitations of the incorporated defects with only the resonance process having the observed temperature dependence. The scattering process would then have an *indirect* temperature dependence in contrast to the case of electronic Raman scattering in which the temperature dependence is caused *directly* by the thermal occupation of the involved electronic states.

Which electronic Raman transitions could be involved in this process? To explain the low energies of the lines only inner transitions in a shallow defect may be considered. Acceptor transitions, as for example found in GaP,[9] ZnTe,[10] or ZnSe (Ref. 11) are unlikely because our samples were all *n* type and thus the acceptor states occupied. In addition, the corresponding transition energies would be too large to fit the experimental findings, leaving thus only inner transitions in shallow donors. The latter also allow a straightforward explanation of the thermalization energies although optically determined activation energies need not be the same as those found in electrical measurements. However, in the case of inner transitions in shallow donors one would expect broader lines and an influence of the free-carrier concentration which we could not observe in our samples.[12,13] The high impurity concentration should lead to the formation of impurity bands resulting in a strong broadening of the lines. In Ref. 2 four of the lines at 189, 237, 151, and 217 cm^{-1} were attributed to an electronic Raman process in which electrons were excited from a deep acceptor level into the excited states of a shallow hydrogenlike donor. One pair of the lines at 189 and 237 cm^{-1} were interpreted as the $1S$-$2S$ and $1S$-$3S$ inner transitions in cubic GaN and the other pair was supposed to belong to the same transitions in the hexagonal modification of GaN, present in their samples as a minority phase. As we already commented, our observation of additional lines with similar temperature and resonance behavior and thus similar origin contradicts this model.[3]

In conclusion, it is obvious that the observed temperature behavior excludes *normal* vibrational Raman scattering as the origin of the defect lines. But two different defect scattering mechanisms are possible: On one hand, electronic Raman scattering on/from donors in which the temperature dependence is caused *directly* by the thermal occupation of the electronic states involved, and, on the other, resonant vibrational Raman scattering on/from the incorporated defects in which the temperature dependence is caused *indirectly* by the resonance mechanism.

In order to clarify the scattering mechanism we performed magnetic-field and pressure-dependent measurements on our samples. The intention was to observe characteristic shiftings and/or splittings of the lines in the case of an electronic Raman-scattering process. Besides, pressure-dependent measurements allowed us to tune continuously the band gap of the material investigated and thus to get further information regarding the resonance process.

B. Magnetic-field dependence

A typical way of distinguishing electronic and vibrational Raman transitions is to measure Raman spectra under high magnetic fields. In case of electronic Raman scattering one would expect to observe characteristic splittings and/or shiftings of the lines in question, as for example in B-doped Se,[14] Li- and As-doped ZnTe,[15] or in the case of crystal-field transitions.[16] Vibrational scattering in contrast should not be affected by an external magnetic field.

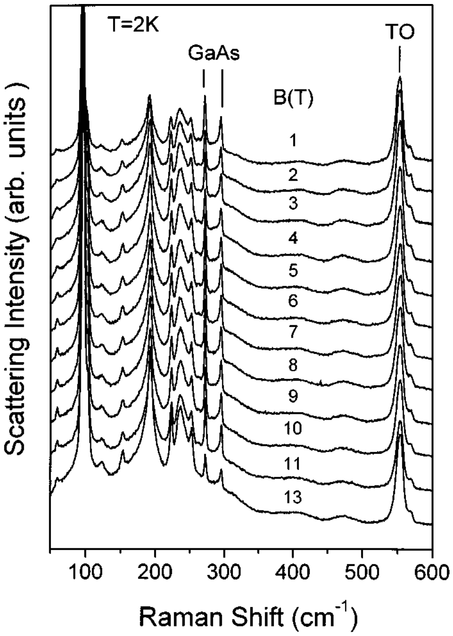

FIG. 6. Low-temperature Raman spectra of GaN/GaAs in dependence on an applied magnetic field [Faraday configuration, $T=2$ K, excitation at 514.5 nm, $z(\ldots)\bar{z}$]. The magnetic field was increased from 1 to 13 T. No change of the spectra could be observed.

Figure 6 shows a series of Raman spectra taken from a GaN/GaAs sample under magnetic fields from 1 to 13 T (Faraday configuration). The temperature was 2 K, the excitation wavelength was at 514.5 nm. The defect modes are clearly visible but neither any splitting nor any shifting of the lines can be seen: $\Delta E = 0.0 \pm 0.2\ \text{cm}^{-1}$. Also, the intensity of the defect modes does not change with the magnetic field. These results strongly indicate that the defect lines are not caused by electronic Raman transitions, e.g., from inner transitions in a donor. One can simply estimate the size of the expected effect. Assuming a g factor of 2 for the *1S* ground state of a donor, as it was found in GaN for shallow donors,[17–20] the applied magnetic field B should lead to a splitting of

$$\Delta E = g \mu B, \tag{2}$$

where μ is the Bohr magneton. A magnetic field of 13 T yields a splitting energy of 1.5 meV=12 cm^{-1}. The experiment in contrast does not show any splitting or shifting of any line. Other electronic transitions can be treated analogously.

Even if one assumes the unlikely case that all defect lines stem from transitions between such electronic states (of one or more donors) that shift equidistantly in a magnetic field one should see a change of the line positions caused by the diamagnetic shift, as e.g., in As-doped ZnTe.[15] Following Larsen[21] the diamagnetic shift of the ground state of a shallow donor is given by

$$\Delta E = \tfrac{1}{2} R^* \gamma^2 \quad \text{with} \quad R^* \gamma^2 = 2.46 \times 10^{-7} \frac{\varepsilon(0)^2}{(m^*/m_0)^3} B^2 \frac{\text{meV}}{T^2}, \tag{3}$$

where R^* is the effective Rydberg energy and γ the reduced magnetic field. In case of an applied magnetic field of 13 T one would expect a change of the ground state of 0.25 meV=2 cm^{-1} which corresponds to a change of 1.5 cm^{-1} for a $1S$-$2S$ transition. A shifting of this size can easily be observed with the setup used in this experiment.

In conclusion, the magnetic-field-dependent Raman study strongly indicates that the defect lines are due to vibrational Raman scattering processes. Because the lines are not affected by an external magnetic field, inner electronic transitions in defects are very unlikely.

C. Pressure dependence

Similar to the study of the magnetic-field behavior measuring the splitting and/or shifting of the lines in question under high hydrostatic pressure gives us more detailed information about the scattering mechanism and about the responsible defects.

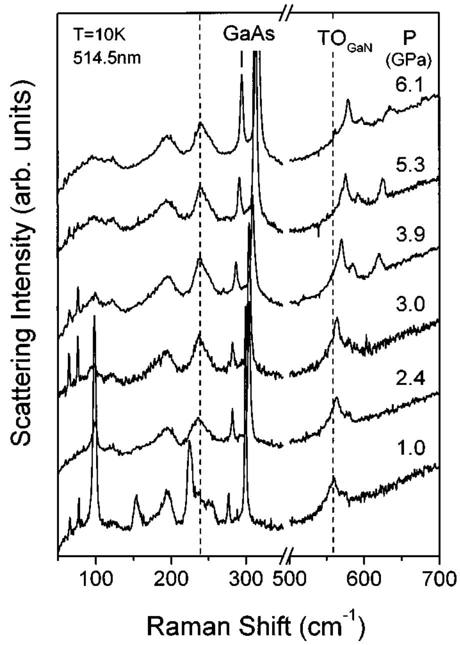

FIG. 7. Series of low-temperature Raman spectra of GaN/GaAs with increasing hydrostatic pressure. The excitation was at 514.5 nm (2.41 eV). While the sharp defect lines disappear for pressures higher than 3 GPa, the two broad defect lines remain present for the whole pressure range. No shifting of the defect lines could be observed.

Figure 7 displays the development of the Raman spectra taken from a GaN/GaAs sample with increasing hydrostatic pressure up to 6.1 GPa. The spectra were normalized to the intensity of the TO mode of GaN. All spectra were recorded at 10 K, the excitation was at 514.5 nm. Already at low pressures the narrow defect lines disappear and only the two broad lines at around 190 and 235 cm^{-1} remain present in the spectra with constant intensity up to 6.1 GPa, but a broad background similar to the broad defect lines remain. It is important to note that in contrast to the host phonon modes the energy position of none of the defect lines change under pressure. Also, the narrow lines do not shift until they disappear. From the constancy of the line positions inner transitions in a shallow defect may be excluded. Applying hydrostatic pressure increases the band-gap energy leading to an increase of the effective mass of the defect. Consequently the energies of inner defect transitions also increase with applied pressure and one would expect a shifting of the Raman lines.

We can easily calculate the magnitude of the expected pressure-induced shifting. In the **k**·**p** approximation a very simple expression for the band-gap dependence of the effective mass of the conduction-band electrons can be derived. When neglecting the coupling to higher bands and under the condition that the band gap E_g is much larger than the spin-orbit splitting[22] one gets[23]

$$\frac{m_0}{m_e^*} \approx \frac{P^2}{E_g}, \tag{4}$$

where P^2 is the coupling matrix element that is nearly constant for most of the III-V and II-VI semiconductors. Thus, the effective mass is proportional to the band gap of the semiconductor. Assuming an effective mass of $m^* = 0.22 m_0$ at atmospheric pressure, as experimentally found for GaN,[24] and an increase of the band-gap energy of 40 meV/GPa,[25,26] the application of 6.1 GPa yields an effective mass of $m^*(6.1\ \text{GPa}) = 0.237 m_0$. The levels of a shallow donor can be calculated like those of a hydrogen atom.[27] We get for the transition energies

TABLE I. Expected shiftings Δ of the defect lines due to the applied hydrostatic pressure in case of inner transitions in a shallow donor.

Transition	$\Delta\omega$ $(P=0)$		$\Delta\omega$ $(P=6.1$ GPa)		Δ
$1S$-$2S$	24.0 meV	194 cm^{-1}	25.7 meV	207 cm^{-1}	13 cm^{-1}
$1S$-$3S$	28.4 meV	229 cm^{-1}	30.4 meV	245 cm^{-1}	16 cm^{-1}

$$\Delta E = Ry \frac{m_e^*}{m_0 \varepsilon(0)^2} (n^{-2} - m^{-2}). \tag{5}$$

Using 9.7 for the dielectric constant $\varepsilon(0)$,[28] we obtain a donor binding energy of 32 meV for atmospheric pressure, which is in good agreement with the experimentally found value of GaN.[29] When applying hydrostatic pressure of 6.1 GPa this value changes to 34.2 meV. According to Eq. (5) we thus expect to see a shifting of the lines if they were caused by inner transitions in such a shallow donor by, e.g., at least 13 cm^{-1} in the case of the line at around 190 cm^{-1}. Table I lists these expected changes for two transitions.

Shifts on the order of 13 cm^{-1} should easily be observed in our experiment (compare the shift of the host phonon modes), but we found no shift at all. The high-pressure study thus confirms the interpretation of our magnetic-field-dependent measurements in that the defect lines cannot be caused by inner electronic transitions in shallow defects.

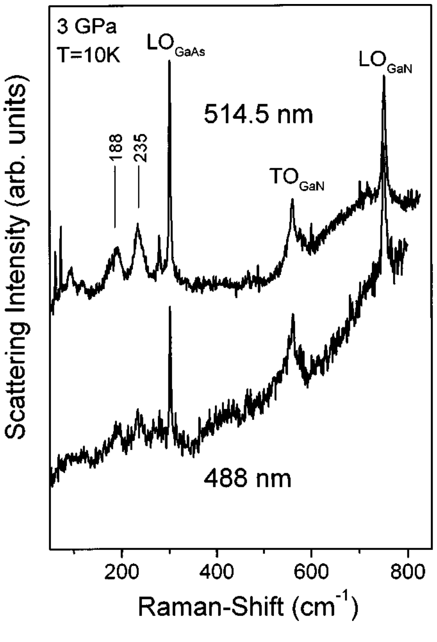

FIG. 8. Two Raman spectra taken at a hydrostatic pressure of 3 GPa. The upper spectrum was excited at 514.5 nm (2.41 eV), the bottom one at 488 nm (2.54 eV). Both spectra were normalized to the intensity of the GaN TO mode.

In addition, we investigated the effect of pressure on the temperature and on the resonance behavior. Our measurements reveal that neither changes significantly. In Fig. 8 we compare two low-temperature Raman spectra taken at 3 GPa. The upper spectrum was excited at 514.5 nm, the bottom spectrum at 488 nm. Both spectra were normalized to the intensity of the TO mode. Although a pressure of 3 GPa was applied to the sample, the defect modes are still much more intense when exciting at 514.5 nm than at 488 nm. This result has an important consequence for the involved resonance states. At first glance a link to those electronic state that are responsible for the yellow luminescence seemed likely because the Raman excitation profile of the defect lines is located in the same energy region. In this interpretation one would already have to consider that the Raman excitation profile should not follow the luminescence but instead the luminescence excitation spectrum because only the latter reflects the energy positions of the involved electronic states. Consequently, one would expect an increase of the resonance profile in the high-energy region, which is not found experimentally (Fig. 5). Our high-pressure measurements confirm these doubts. They demonstrate that the resonance states of the defect modes can neither belong to the yellow luminescence nor to any states related to the conduction band. In both cases one would expect a shifting of the resonance profile of approximately 120 meV, based on the experimentally found pressure coefficient of 40 meV/GPa,[25,26] which is equal to the difference in the excitation energies used to obtain the two spectra in Fig. 8. If a shallow defect or the conduction band were involved in the resonance process one would expect the opposite intensity distribution. The defect lines should be more intense in the spectrum excited at 488 nm than in the spectrum excited at 514.5 nm. In conclusion, no shallow states can be involved in the resonance process.

D. As impurities in GaN: Influence of the substrate

After clarifying the principle scattering mechanism we now turn to the identification of the responsible defects. We performed measurements on several series of undoped GaN layers grown on different substrates and by different growth techniques (MBE, MOCVD, HVPE). The defect lines were present only in those spectra that were taken from GaN layers deposited on GaAs substrates. We thus assumed that the incorporation of As from the substrate into the layer might form defects that are responsible for the lines in question. To prove our assumption we measured GaN layers grown on sapphire that were intentionally doped with As. Secondary-ion mass spectroscopy (SIMS) revealed an As concentration of around 10^{18} cm^{-3} in this layer, which is in the same range of the As concentration in our GaN/GaAs samples.[30] A spectrum taken from one of these samples after excitation at 514.5 nm is shown in Fig. 9. The strongest lines are located at 96, 178, and 235 cm^{-1}. The broad background below 300 cm^{-1} is due to disorder-induced scattering and can also be observed in GaN/GaAs and in ion-damaged GaN.[31] The energy positions are in very good agreement with the lines known from the GaN/GaAs samples. The lines also exhibit the same temperature behavior. They decrease nearly exponentially in intensity with increasing temperature. The activation energies are between 10 and 60 meV, i.e., in the same range as the lines known from the GaN/GaAs samples. We are thus certain that these lines have the same origin and that the incorporation of As into the GaN layer leads to the responsible defects. It remains unclear whether As is directly involved, i.e., whether the defect contains As, or As acts only as a catalyst.

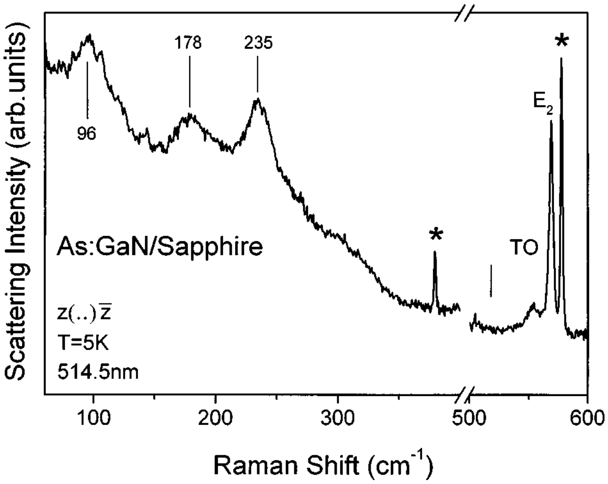

FIG. 9. Low-temperature Raman spectrum of an As-doped GaN layer grown on sapphire. Three of the defect modes at 96, 178, and 235 cm^{-1} occur. The asterisks denote lines of the sapphire substrate. The temperature was 5 K, the excitation wavelength was 514.5 nm (2.41 eV).

We also investigated Si-, C- and Mg-doped GaN samples grown on sapphire, but we did not observe any of the defect lines. It is noteworthy that the resonance behavior differs slightly from the one in GaN/GaAs, in that the narrower lines at 95 and 105 cm^{-1} are even more intense when excited in the red spectral region.

In addition, the comparison of several series of differently/diversely grown samples corroborate our finding from the high-pressure Raman measurements. There cannot be a direct link to the yellow luminescence. Otherwise one would expect the observation of the defect lines from nearly every sample.

IV. DISCUSSION AND CONCLUSIONS

Summarizing our results, the low-energy Raman lines cannot stem from the host GaN or substrate lattice. Neither disorder-activated scattering nor second-order Raman scattering can explain their energy positions and their small linewidths. We thus related these lines to excitations of built-in defects. This is confirmed by the unusual temperature behavior. As the comparison of several series of sample showed, the lines occur only in samples grown on GaAs. The lines may also be detected in GaN layers grown on sapphire when doping these layers with As thus clearly showing that they are associated with As-related defects. The lines decrease drastically in intensity with increasing temperature and vanish at room temperature excluding normal vibrational Raman scattering as their origin. This temperature behavior can be explained by two opposite types of defect-scattering mechanisms: Either the lines originate from electronic Raman transitions in which the thermal occupation of the involved electronic defect states serves for the temperature dependence or the lines are caused by resonant vibrational Raman scattering (resonant modes) in which only the resonance process exhibits the thermalization. Our magnetic-field-dependent and pressure-dependent Raman measurements clarified this point. Because no splitting nor shift was observed in these measurements, inner electronic transitions of defects are very unlikely. Thus, our results strongly indicate a resonant vibrational Raman process, with only the resonance having the observed temperature behavior.

As demonstrated by our doping study and by the comparison of differently grown samples it is obvious that the defects are associated with As impurities. Although we cannot definitely say whether the defects contain As or the incorporated As impurities leads only to the formation of these defects, we believe that the defect lines stem from vibronic excitations related to As complexes. Bulk As does indeed have vibrational modes in the same frequency range. The rhombohedral lattice of As with two atoms per unit cell has three Raman-active zone-center modes. The A_{1g} mode is found in the range 253–257 cm^{-1}, the twofold degenerate E_g mode is located at 193–197 cm^{-1}.[32–34]

The pressure-dependent measurements give us further information on the type of defect. Usually, the application of hydrostatic pressure leads to a hardening of the vibrational modes or in case of instability and phase transformation to a softening of modes.[35] But we found no shift of any defect line. This constancy can only be explained by scattering from defects, which do not feel the surrounding pressure. Therefore, normal local modes, in which As atoms are placed either on the Ga or N sites, may be excluded. Possible defect candidates are vacancies or atoms captured inside a vacancy or inside of any kind of cage that protects the defects from the applied pressure. The gallium vacancies in GaAs for example do not show any pressure dependency.[36] We thus suggest that the defect lines originate from incorporated As impurities formed to complexes located inside of microscopic cages of the surrounding GaN. These are possibly Ga vacancies. From the different linewidths of the defect modes one may also conclude that the two broad lines at 190 and 235 cm^{-1} may be attributed to a defect cluster, whereas the sharper lines may be excitations of isolated As defects.[37]

Although at first glance it appeared likely, there is no link to the yellow luminescence, as shown by the pressure measurements and by the comparison of differently grown samples. The pressure measurements also made it clear that no shallow state can be involved in the resonance process. There remain only deep states in the GaN host crystal formed by the As impurities. Recent publications on As-doped GaN confirms that As forms deep states.[38]

In conclusion, we showed that the defect lines, which appear in the Raman spectra as sharp and intense lines in the low-energy region form 95 to 250 cm^{-1}, are caused by incorporated As impurities in the GaN lattice. Although their temperature behavior indicated an electronic Raman-scattering process, our pressure- and magnetic-field-dependent measurements definitely show that they are of vibrational origin, most likely resonant modes of As complexes in the GaN layers.

V. ACKNOWLEDGMENTS

The authors are indebted to all growth teams, especially D. J. As, D. Schikora, and B. Schöttker for providing the GaN/GaAs samples. We also thank K. Syassen for the help with the pressure measurements and I. Loa and P. Thurian for the assistance during the magnetic-field-dependent measurements.

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