

Defect Modes and Disorder-Induced Raman Scattering in GaN*

By H. Siegle, I. Loa, P. Thurian, G. Kaczmarczyk, L. Filippidis,
A. Hoffmann, C. Thomsen

Institut für Festkörperphysik, Technische Universität Berlin, D-10623 Berlin, Germany

D. Schikora, M. Hankeln and K. Lischka

Institut für Optoelektronik, Universität Paderborn, D-33095 Paderborn, Germany

(Received September 10, 1996)

Raman scattering / Semiconductors / GaN / Defects / Disordering

We present results of Raman-scattering experiments on GaN layers with different ratios of cubic and hexagonal phase grown on GaAs and sapphire. In the low-energy region ($60\text{--}250\text{ cm}^{-1}$) we found a series of sharp modes which increase exponentially in intensity with decreasing temperature. The modes disappear when reaching room temperature. Wavelength-dependent measurements reveal that they are strongest under excitation at around 568 nm. No magnetic-field dependence could be observed. From their exclusive presence in GaN layers grown on GaAs, we conclude that they are likely to be caused by As-defects in GaN or N-impurities in GaAs. Apart from the host phonon modes in the high-energy region we found a broad band ranging from the cubic TO to the LO phonon frequencies, which is caused by disorder-induced scattering.

1. Introduction

In the last few years the wide-bandgap semiconductor GaN has received increasing attention because of its applications for optoelectronic devices working in the blue to ultraviolet spectral region [1]. At equilibrium, GaN crystallizes in the wurtzite structure only. By adjusting the growth conditions molecular beam epitaxy allows to grow also cubic layers [2]. Cubic GaN can be advantageous over the usual hexagonal phase in that an optical cavity for lasing is easily obtained by cleaving.

In spite of recent impressive technological achievements culminating very recently in the realization of the first GaN-based laser diode [3], there are a lot of questions about the basic physical properties of GaN compared to other III–V semiconductors. Only little effort has been made to analyze

* Presented at the 13th International Symposium on Electrons and Vibrations in Solids and Finite Systems (Jahn-Teller Effect) Berlin 1996.

the lattice dynamics of GaN. Raman spectroscopy is a powerful tool to study the lattice dynamics and to get information about electron-phonon interaction and incorporated defects in the material investigated.

We present results from Raman-scattering experiments on GaN layers on different substrates. One series of samples was grown on GaAs with different ratios of cubic and hexagonal phase. Another series of pure hexagonal layers was deposited on sapphire. When cooling the layers grown on GaAs down to temperatures below 100 K a series of sharp low-energy modes appear. In order to study these modes we performed temperature-, wavelength-, and magnetic field-dependent Raman measurements.

2. Experiment

The samples under study were two series of GaN grown on GaAs and sapphire, respectively. The 1 μm thick GaN layers with different hexagonal phase content were deposited on GaAs by molecular beam epitaxy (MBE). The layers on sapphire were grown by metal organic chemical vapor deposition (MOCVD) and hydride vapor phase epitaxy (HVPE). Their thicknesses vary between 2 μm and 400 μm .

The Raman-scattering experiments were carried out in backscattering geometry with a Dilor triple-grating spectrometer equipped with a cooled charge-coupled device (CCD) detector. An Ar⁺-Kr⁺ mixed-gas laser was used for excitation. Parts of the experiments were performed with a microscope setup focussing the laser beam on a point spot with a diameter of about 1 μm . The sample temperature was varied in the range from 4.2 K to 300 K using a microscope cryostat. Magnetic-field dependent measurements up to 13 T were performed with a split-coil magnet, in which the sample was immersed in liquid Helium.

3. Experimental results and discussion

a) Defect modes

In Fig. 1a low-temperature Raman spectra taken from a hexagonal GaN layer grown on sapphire (upper curve) and from a cubic layer grown on GaAs (lower curve) are compared. While the upper spectrum shows only the phonon modes of hexagonal GaN located at 145 cm^{-1} , 569 cm^{-1} (both E_2) and at 735 cm^{-1} ($A_1(\text{LO})$), the lower spectrum exhibits in addition to the cubic TO and LO mode (at 555 cm^{-1} and 740 cm^{-1}) a series of sharp modes in the low-energy part of the spectrum. In total, we observed nine modes ranging from 60 cm^{-1} to 250 cm^{-1} , which are shown on an enlarged spectral scale in Fig. 1b.

The temperature dependence of these modes is displayed in Fig. 2. The intensity of all the additional low-energy modes increases drastically for

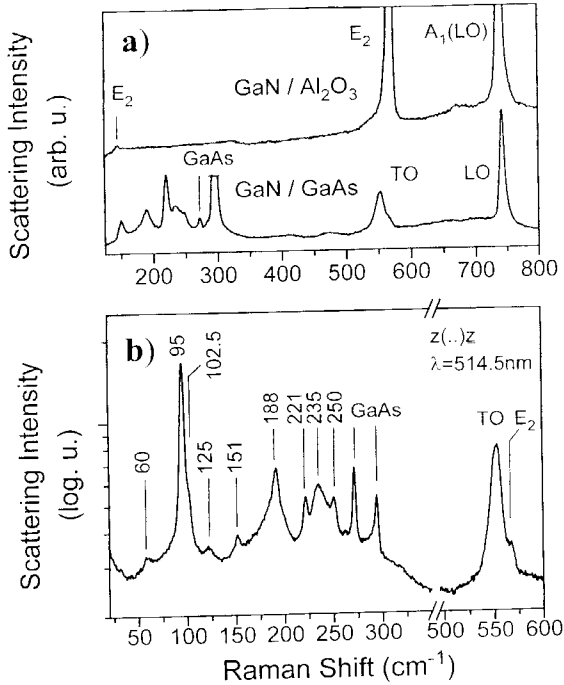


Fig. 1. a) Comparison between the low-temperature (4.2 K) Raman spectra of a GaN layer grown on sapphire (upper curve) and on GaAs (bottom curve). While the spectrum of the hexagonal layer grown on sapphire exhibits only the phonon modes of the host material, a series of defect modes are present in the cubic layer grown on GaAs. Excitation was at 514.5 nm. b) Low-temperature Raman spectrum taken from GaN grown on GaAs after excitation at 514.5 nm on an enlarged spectral scale.

temperatures lower than 100 K. Plotting the logarithmic intensities versus the inverse sample temperature, as it is done exemplarily for two modes in Fig. 3, we find a good fit to the expression

$$I \propto \frac{1}{1 + C \exp\left(-\frac{E_{\text{act}}}{kT}\right)}, \quad (1)$$

where C is a constant and E_{act} an activation energy. This behavior cannot be explained by vibrational Raman scattering and indicates that these modes are caused by electronic Raman scattering, e.g. inner transitions between shallow donor or shallow acceptor states [5]. Assuming such an electronic origin one would expect a change in energy when applying a magnetic field. We performed magnetic-field dependent Raman-scattering experiments on our samples up to 13 T, but we could not observe any shifting of the modes.

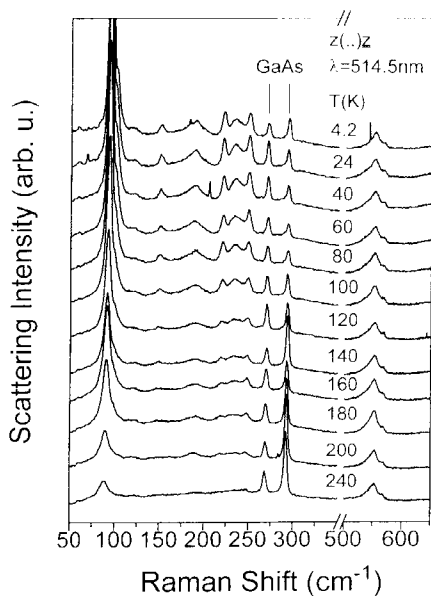


Fig. 2. Series of Raman spectra taken from GaN grown on GaAs at temperatures between 4.2 K and 240 K. The intensity increases strongly with decreasing temperature.

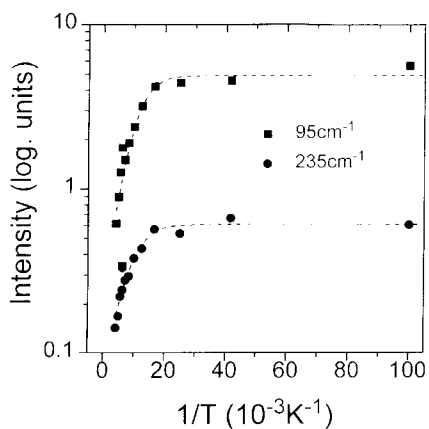


Fig. 3. Logarithmic intensity of two defect-correlated peaks located at 95 cm^{-1} and 235 cm^{-1} as a function of inverse sample temperature. The dashed curves result from fits using Eq. (1).

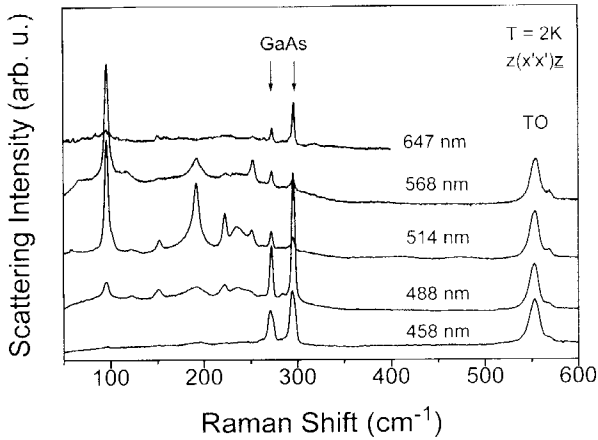


Fig. 4. Low-temperature (2 K) Raman spectra obtained with different excitation wavelengths between 458 nm and 647 nm.

In Fig. 4 low-temperature Raman spectra excited at wavelengths between 458 nm and 647 nm are shown. The intensities of the low-energy modes vary strongly and exhibit clearly a resonant behavior with a maximum between 514.5 nm and 568 nm.

The low-energy modes observed can be explained by Raman scattering by defects incorporated in the host material, but the exact scattering process remains unclear. From the temperature behavior Ramsteiner *et al.* concluded that the modes were caused by transitions between the hydrogen-like electronic states of a shallow donor in GaN [5] but the magnetic-field independence makes this explanation doubtful. Furthermore, we found additional modes located at lower energies (60 cm^{-1} , 95 cm^{-1} , 102.5 cm^{-1} , 125 cm^{-1}) which were not reported in Ref. [5]. All these lines show a similar resonance and temperature behavior, but do not fit the model published by Ramsteiner *et al.* From the fact, that the defect modes were only present in spectra taken from layers grown on GaAs, we believe that either N-impurities in GaAs or As-defects in GaN are likely to be their origin [6].

b) Disorder-induced Raman scattering

By adjusting the growth conditions MBE allows to grow either cubic or hexagonal GaN layers. We performed Raman-scattering experiments on a series of such layers grown on GaAs with different ratios of cubic and hexagonal phase. The different polarisation scattering selection rules and the slightly different phonon frequencies allow us to distinguish the two phases and to determine the content of hexagonal phase in predominantly cubic samples and vice versa [4]. In Fig. 5 room-temperature Raman spectra

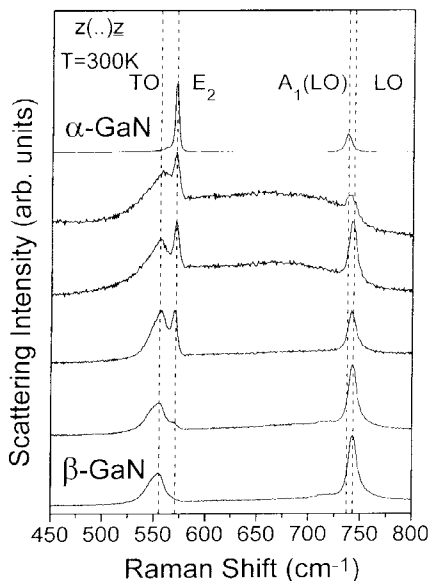


Fig. 5. Micro-Raman spectra taken at room temperature on a series of GaN layers grown on GaAs with different ratios of cubic and hexagonal phase. Excitation was at 514.5 nm.

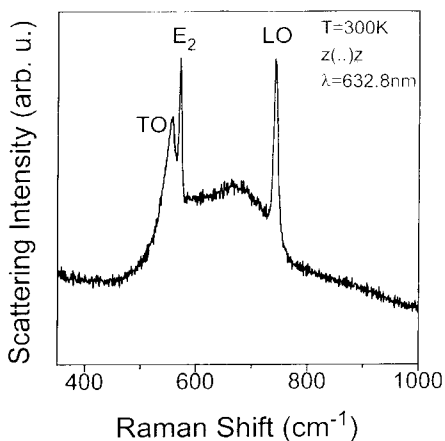


Fig. 6. Room-temperature Raman spectrum of a GaN layer with mixed phase content. The broad background signal between the TO and LO mode is caused by disorder in the layer.

taken on samples with different ratios of hexagonal and cubic phase are compared. The varying intensity of the hexagonal E_2 mode reflects the hexagonal phase content. When both modifications coexist a broad band ranging from the cubic TO to the LO phonon frequencies appears (see Fig. 6). The band is strongest for the second curve from top in Fig. 5 where from the LO peak frequency we know that the cubic and hexagonal phase are present in similar amounts [4]. The sharp cut-offs of this band at the TO and LO frequencies indicate that it is caused by disorder-activated Raman scattering, because in disordered materials, the absence of long-range order yields to a breakdown of the $\mathbf{q} = \Delta\mathbf{k} \approx \mathbf{0}$ selection rule, where \mathbf{q} is the wavevector of the phonon and $\Delta\mathbf{k}$ the difference between incident and scattered photon wavevectors [7]. Thus, the Raman spectrum reflects the vibrational density of states.

4. Summary

We found a series of sharp modes in the range between 60 cm^{-1} and 250 cm^{-1} for temperatures below 100 K. The intensity of these modes increases drastically with decreasing temperature. Raman excitation spectra show a maximum between 514.5 nm and 568 nm. No magnetic-field dependence was observed. The modes were only present in GaN layers grown on GaAs. From this we believe that either As-defects in GaN or N-impurities in GaAs are likely to be their origin.

Apart from the low-energy modes we found a broad band ranging from the cubic TO to the LO phonon frequencies, which is strongest when both modifications coexist. From the sharp cut-off at the TO and LO frequencies one can conclude that this broad band is caused by disorder-activated scattering.

References

1. For a review, see e.g. R. F. Davis, Proc. of IEEE **79** (1991) 702; S. Strite and H. Morkoc, J. Vac. Sci. Technol. **B10** (1992) 1237; H. Morkoc, S. Strite, G. B. Gao, M. E. Lin, B. Sverdlov and M. Burns, J. Appl. Phys. **76** (1994) 1363.
2. O. Brandt, H. Yang, B. Jenichen, Y. Suzuki, L. Daweritz and K. H. Ploog, Phys. Rev. B **52** (1995) R2253.
3. S. Nakamura, Jap. J. Appl. Phys. **35** (1996) L74.
4. H. Siegle, L. Eckey, A. Hoffmann, C. Thomsen, B. K. Meyer, D. Schikora, M. Hankeln and K. Lischka, Solid State Commun. **96** (1995) 943.
5. M. Ramsteiner, J. Menninger, O. Brandt, H. Yang and K. H. Ploog, Appl. Phys. Lett. **69** (1996) 1276.
6. H. Siegle, I. Loa, P. Thurian, L. Eckey, A. Hoffmann, I. Broser and C. Thomsen, Appl. Phys. Lett., submitted.
7. M. H. Brodsky, in *Light Scattering in Solids I*, edited by M. Cardona (Springer, Berlin 1975), pp. 205.