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RAMAN SCATTERING FROM DEFECTS IN GaN

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Abstract. We present results from Raman-scattering experiments on GaN layers grown on GaAs and sapphire. In the low-energy region between 95 cm^{-1} and 250 cm^{-1} a series of sharp lines appear which decreases exponentially in intensity with increasing temperature. The lines disappear when reaching room temperature. Wavelength-dependent measurements reveal that they are strongest under excitation at around 514.5 nm. Raman-scattering experiments at high pressures up to 6 GPa show that neither their energies nor their resonance profile vary remarkably with pressure indicating that they are not connected to the bandgap. Comparitive measurements on different substrates show that these lines are exclusively present in GaN layers grown on GaAs.

Introduction.

In the last few years the wide-bandgap semiconductor GaN has received increasing attention because of its application as the favorite basic material for optoelectronic devices working in the blue to ultraviolet spectral region [1]. One of the main problems which still restricts the growth of high-quality GaN layers is the high concentration of defects which yields high background carrier concentrations and the typical n-type conductivity of GaN layers. It is still unclear what kind of defects are responsible for these effects.

We present results of Raman-scattering experiments on predominantly cubic GaN layers grown on GaAs and hexagonal layers grown on sapphire. While the layers deposited on sapphire exhibit only the expected host phonon modes, we found a series of additional sharp lines in the range between 95 cm^{-1} and 250 cm^{-1} from the layers grown on GaAs. Four of these lines have already been observed by Ramsteiner et al. [2]. The lines show a strong temperature dependence. They decreases drastically in intensity when increasing the sample temperature and disappear when reaching room temperature. Wavelength-dependent measurements show that they have a broad resonance profile with its maximum around 514.5 nm. Ramsteiner et al. [2] attributed four of the observed lines to hydrogen-like transitions between the electronic states of a shallow donor in hexagonal and cubic GaN. In order to prove this model we performed a systematic Raman study on several series of GaN layers grown on GaAs and sapphire. We found that more lines appear than expected by hydrogen-like transitions of one donor [2, 3]. On the basis of the new experimental data including results of high-pressure Raman experiments we discuss possible candidates of defects.

Experimental Details.

The samples under study were series of predominantly cubic GaN layers grown on (001) GaAs using molecular beam epitaxy (MBE) and several hexagonal layers grown on sapphire by MBE,

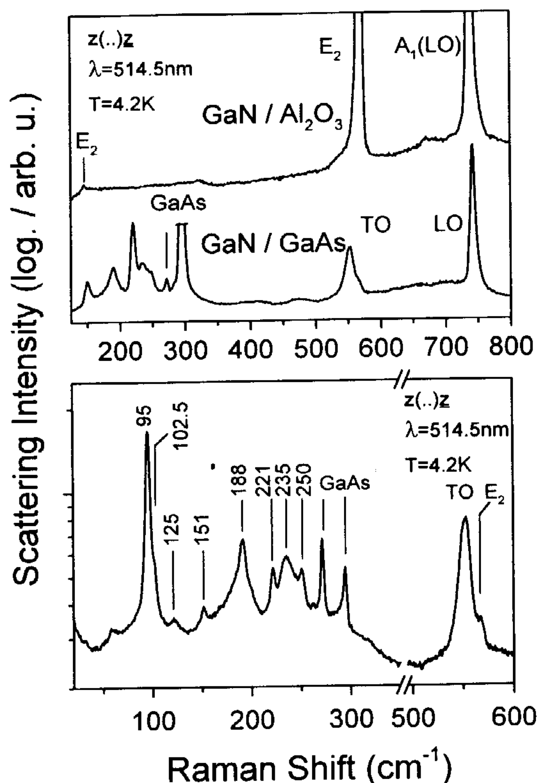

Fig. 1a: Comparison between the low-temperature (4.2 K) Raman spectra of a GaN layer grown on sapphire (upper curve) and on GaAs (bottom curve). While the spectrum of the hexagonal layer grown on sapphire exhibits only the phonon modes of the host material, a series of defect modes are present in the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

Fig. 1b: Low-temperature Raman spectra taken from GaN grown on GaAs after excitation at 514.5 nm on an enlarged spectral scale.

metal organic chemical vapor deposition (MOCVD) and hydride vapor phase epitaxy (HVPE). Thicknesses vary between 0.5 to 2 μm in case of the MBE samples and up to 400 μm in case of the HVPE samples.

The Raman-scattering experiments at ambient conditions were carried out in back-scattering geometry with a triple-grating spectrometer equipped with a cooled charge-coupled device (CCD) detector. An Ar^+/Kr^+ mixed-gas laser was used for excitation in the range between 458 nm and 647 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 from 2 K to 300 K using either an Oxford microscope cryostat in case of micro-Raman measurements or an Oxford bath cryostat.

The high-pressure Raman experiments were performed in a gasketed diamon-anvil cell at low temperatures (10 K) using liquid helium as the pressure-transmitting medium. The shift of the

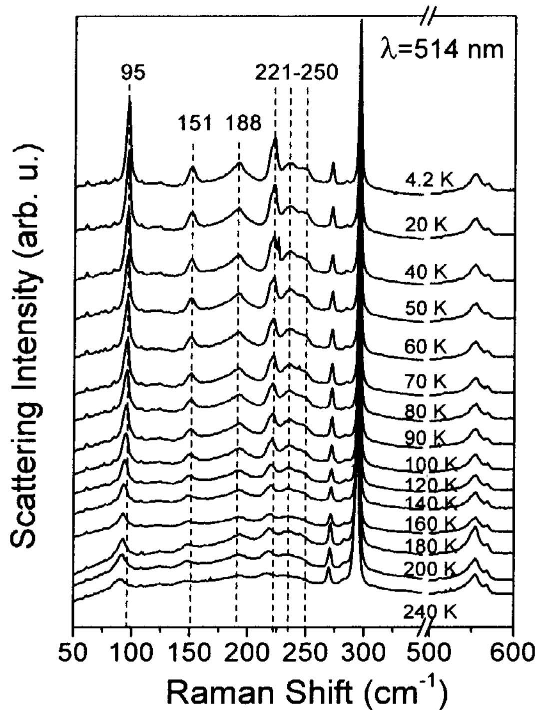

Fig. 2: Evolution of the Raman spectra taken from a GaN layer grown on GaAs with temperature. The defect modes show a strong decrease in intensity with increasing temperature.

ruby R-line luminescence was used to calibrate the pressure inside the cell. Prior to the experiment, the substrates of the samples were mechanically removed. Finally, the samples were cleaved and placed in the gasket hole of the diamond-anvil cell. The 488 nm, 502 nm and 514.5 nm lines of an Ar^+-ion laser were used for excitation. Like in the experiments at ambient conditions the scattered light was detected in back-scattering geometry and analyzed by a triple-grating spectrometer equipped with a CCD.

Results and Discussion.

In Fig. 1a typical 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 Raman modes of the hexagonal GaN phonons located at 145 cm^{-1} (E_2(low)), 569 cm^{-1} (E_2(high)) and at 735 cm^{-1} (A_1(LO)), the lower spectrum exhibits in addition to the host phonon modes of cubic GaN (TO at 555 cm^{-1} and LO at 740 cm^{-1}) a series of sharp lines in the low-energy part of the spectrum. In total we observe eight lines ranging from 95 cm^{-1} to 250 cm^{-1}, which are shown on an enlarged scale in Fig. 1b.

The temperature dependence of these modes is displayed in Fig. 2. The intensity of all the additional low-energy modes decreases drastically when increasing the sample temperature and finally disappear when reaching room temperature. This behavior cannot be explained by vibrational Raman scattering and indicates that these modes are caused by electronic Raman scattering from defects built in the host material [4].

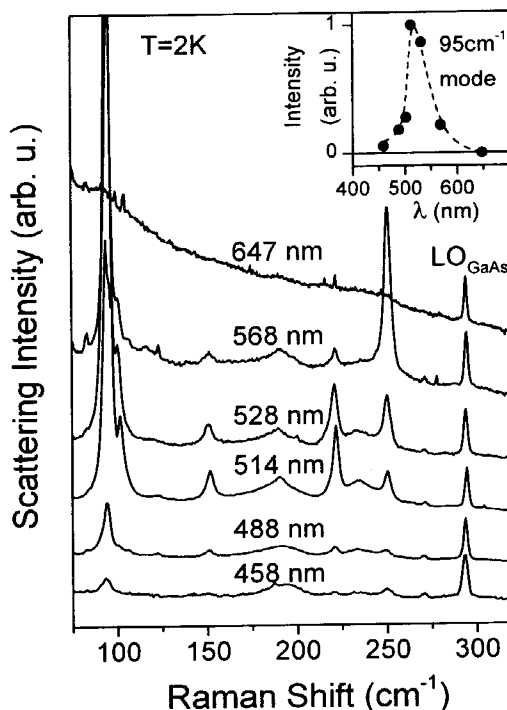

Fig. 3: Low-temperature Raman spectra obtained with different excitation wavelengths between 458 nm and 647 nm. The inset shows examplary the resulting resonance profile of the 95 cm^{-1} mode. The dashed line is only guide to the eye.

Four of these defect modes were also found by Ramsteiner et al. [2]. From the temperature behavior Ramsteiner et al. concluded that these four modes were caused by transitions between the hydrogen-like electronic states of a shallow donor in GaN. They ascribed the lines at 188 cm^{-1} and 235 cm^{-1} to inner transitions of one shallow donor in cubic GaN and the lines at 151 cm^{-1} and 221 cm^{-1} to a corresponding donor in the hexagonal modification which was present in their samples as a minority phase. We found a series of additional lines from which three (95 cm^{-1}, 102.5 cm^{-1} and 125 cm^{-1}) are located at lower energies and thus do not fit a hydrogen-like donor.

Figure 3 shows low-temperature Raman spectra of a GaN film excited at different wavelengths in the range from 458 nm to 647 nm. The intensities of the defect modes vary strongly and exhibit clearly a resonant behavior with a maximum around 514. 5 nm as can be seen for the 95 cm^{-1} mode in the inset of Fig. 3. All defect modes show a similar temperature and resonance behavior [3]. From this it seems clear that all these lines should either have a similar origin or the electronic states involved in the resonance mechanism should be the same. One single donor can be ruled out as an explanation.

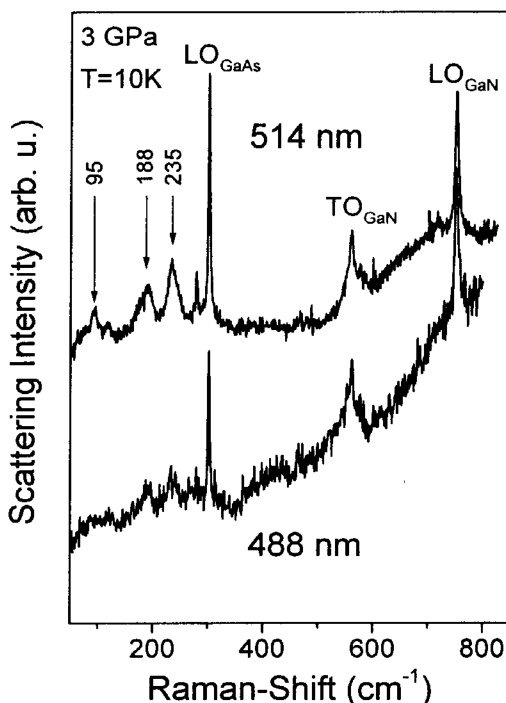

Fig. 4: Raman spectra taken at a hydrostatic pressure of 3 GPa and different excitation wavelengths.

It is in principle possible to determine activation energies of the defect modes by fitting their intensity as a function of temperature. We found that the activation energies ranging from 10 meV to 50 meV differ from mode to mode and depend strongly on the wavelength used for excitation [3, 5] confirming that the various modes could not belong to one single shallow impurity.

In order to get further information on the nature of the responsible defects we have performed magnetic-field dependent Raman-scattering experiments on our samples up to 13 T. Assuming an electronic origin one would expect a change in energy when applying a magnetic field, but we could not observe any shift of the lines [6].

In contrast, the application of high hydrostatic pressures on these samples changes the Raman spectra drastically as displayed in Fig. 4, in which two Raman spectra at 3 GPa with different excitation wavelengths are compared. One was excited at 514.5 nm the other at 488 nm. Both spectra were normalized to the intensity of the GaN LO phonon mode. When applying hydrostatic pressure the intensity of the sharp lines at 95 cm^{-1}, 151 cm^{-1}, 221 cm^{-1} and 250 cm^{-1} decreases strongly without changing their energy position remarkably. Finally these lines disappear for pressures higher than 3 GPa. As can be seen in Fig. 4 the strongest defect mode at 95 cm^{-1} could only weakly be observed. However, the broader lines at 188 cm^{-1} and 235 cm^{-1} seems not to be affected by pressure and they are still present in the spectra up to 6 GPa.

If the electronic states involved in the resonance mechanism were connected to the bandgap one would expect that the lines should be stronger in the spectrum excited at 488 nm than at

514.5 nm, because of the positive pressure coefficient of the GaN bandgap, which is about 40 meV/GPa [7]. Following this relation the resonance maximum at 3 GPa should be located 120 meV higher in energy, corresponding to a change from 514.5 nm to 488 nm. We found that the intensity ratio between the lines excited at these different wavelengths does not change, indicating that the defects responsible for the resonant behavior are not connected to the bandgap but form strongly localized states. Because additionally the energy positions of the defect modes do not change with increasing pressure, inner transitions between the electronic states of shallow impurities can also be ruled out as an explanation for the observed lines.

Probably, deep impurities are involved in the electronic resonance transitions but the chemical identification of these defects remains unclear from our results. However, they must be specific to the MBE growth process of GaN layers on GaAs substrates, because the defect modes were exclusively present in these films.

Conclusion.

Low-temperature Raman measurements were performed on several series of GaN films epitaxially grown on GaAs and sapphire by MBE, MOCVD and HVPE. Only those GaN layers which were deposited on GaAs exhibit a series of sharp lines in the low-energy range from 95 cm^{-1} to 250 cm^{-1}. The intensity of these defect modes increases drastically with decreasing temperature indicating an electronic scattering origin. Raman excitation spectra show a maximum around 514.5 nm. High-pressure Raman experiments reveal that the responsible defects are strongly localized. Their exclusive presence in GaN films on GaAs indicates that they are connected to the growth procedure and to the substrate.

Acknowledgements

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References.

1. For a review see e.g. R. F. Davis, Proc. IEEE **79**, 702 (1991); S. Strite and H. Morkoc, J. Vac. Sci. Technol. **B10**, 1237 (1992)
2. M. Ramsteiner, A. J. Menninger, O. Brandt, H. Yang, and K. H. Ploog, Appl. Phys. Lett. **69**, 1276 (1996)
3. H. Siegle, I. Loa, P. Thurian, L. Eckey, A. Hoffmann, I. Broser, and C. Thomsen, Appl. Phys. Lett. **70**, 909 (1997)
4. M. V. Klein, in: Light Scattering in Solids I, ed. M. Cardona (Springer, Berlin, Heidelberg 1983), pp. 147
5. H. Siegle et al., to be published
6. H. Siegle, I. Loa, P. Thurian, G. Kaczmarczyk, L. Filippidis, A. Hoffmann, C. Thomsen, D. Schikora, M. Hankeln, K. Lischka, Zeitschrift für Physikalische Chemie 200, **187** (1997)
7. T. Suski, P. Perlin, H. Teisseyre, M. Leszcynski, I. Grzegory, J. Jun, M. Bockowski, S. Porowski, and T. D. Moustakas, Appl. Phys. Lett. **67**, 2188 (1995)