Proc. ICPS 23, Berlin, Germany, 1996, ed. M.Scheffler, R. Zimmermann
p. 537

ACOUSTIC AND OPTICAL ZONE-BOUNDARY PHONONS IN GALLIUM NITRIDE

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We present results from second-order Raman-scattering experiments on hexagonal and cubic GaN covering the acoustic and the optical overtone spectral region. Comparing our calculated phonon dispersion curves under consideration of the experimentally obtained and group-theoretically derived selection rules we were able to assign the observed structures to particular phonon branches and determined the points in the Brillouin zone from which the scattering originates. Our measurements reveal for the first time the energies of acoustic zone-boundary phonons and of the silent B modes in hexagonal GaN.

Only little effort has been made to analyze the lattice dynamics of GaN. Since large enough single crystals are not yet available for neutron-scattering studies, we have performed second-order Raman-scattering experiments on hexagonal and cubic GaN. In contrast to first-order Raman measurements second-order experiments provide information on the vibrational states in the entire Brillouin zone. We have used all necessary scattering geometries to obtain selection rules and have performed a calculation of the dispersion curves. The spectral region investigated contains the acoustic as well as the optical overtone and combination part. Thus, we could obtain, to our knowledge for the first time, the energies of zone-boundary acoustic phonons in both modifications of GaN and additionally the silent B modes of hexagonal GaN. Using group-theoretically derived selection rules in combination with calculated dispersion curves we assigned the observed peaks to particular phonon branches and determined the points in the Brillouin zone from which the scattering originates.

The samples investigated were 1μm thick layers of cubic GaN grown on (001) GaAs by molecular beam epitaxy and 200-400μm thick hexagonal layers grown on sapphire using hydride vapor phase epitaxy. The Raman-scattering experiments were carried out in backscattering geometry using a Micro-Raman spectrometer with a charge-coupled device detector. The 514.5nm line of an Ar^+ laser and the 632.8nm line of a He-Ne laser were used for excitation. The spectral resolution was about 1cm^{-1}.

Figure 1 shows an overall view of a room-temperature second-order Raman spectrum of a hexagonal (upper curve) and a cubic (bottom curve) GaN layer taken in $z(..)\bar{z}$ geometry (corresponding to A_1+E_2 symmetry). Apart from the strong first-order modes at 569cm^{-1} (E_2) and at 735cm^{-1} (A_1(LO)) of the hexagonal material and at 555cm^{-1} and 742cm^{-1} of the cubic material[1] a

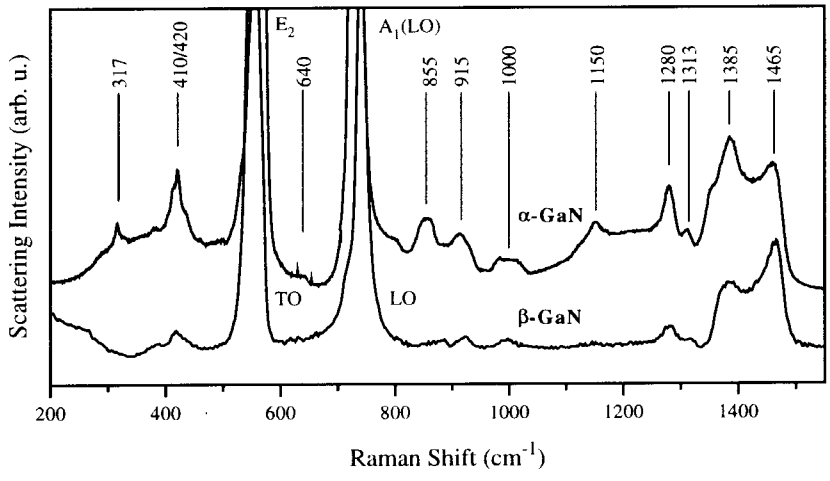

Figure 1: Second-order Raman spectrum of hexagonal (upper curve) and cubic (bottom curve) GaN grown on sapphire taken at room temperature in backscattering geometry $z(..)\bar{z}$.

rich structure originating from second-order scattering processes can be seen. In the following we discuss the strongest structures of hexagonal GaN under consideration of our calculated phonon dispersion curves and compare these hexagonal features with modes observed in cubic GaN.

The low-frequency region (approximately 200-650cm^{-1}) is dominated by acoustic overtones. In the hexagonal spectrum two strong Raman bands were observed, one located at 317cm^{-1} and one doublet at 410cm^{-1} and 420cm^{-1}. As can be seen in the phonon dispersion curves of hexagonal GaN in Fig. 2, which were calculated by a modified valence-force model of Kane [2,3], the energy position of the 317cm^{-1} mode fits well with the flat phonon branch at the H-point in the Brillouin zone. The observed A_1 symmetry also corresponds to the symmetry predicted by group theory of an overtone scattering process at this point in the Brillouin zone [4]. This is emphasized by the fact that this mode was not observed in cubic GaN (see bottom curve in Fig. 1). The doublet around 415cm^{-1} also originates from acoustic phonons. Comparing the calculated phonon dispersion curves (Fig. 2) the doublet can be attributed to an overtone of transverse acoustic phonons either at the symmetry point A, K or M in the Brillouin zone. The energy position as well as the symmetry expected from the group-theoretical selection rules fit together with the experimental observation. The dispersion curve runs flat at this point, consequently the density of phonon states is high. According to the selection rules we can attribute the mode at 410cm^{-1} which exhibits A_1 symmetry to the A- or K-point while the higher-energy portion of the doublet, exhibiting A_1+E_2 symmetry,

belongs to the M-point. As can be seen in Fig. 1 this mode was also observed in cubic GaN. The hexagonal mode lying between the first-order peaks at around 640cm^{-1} can be attributed to an overtone process of the highest acoustic phonon branch at the zone-center which agrees well with our calculation. The strongest features of the middle-frequency region (650-1000cm^{-1}) of

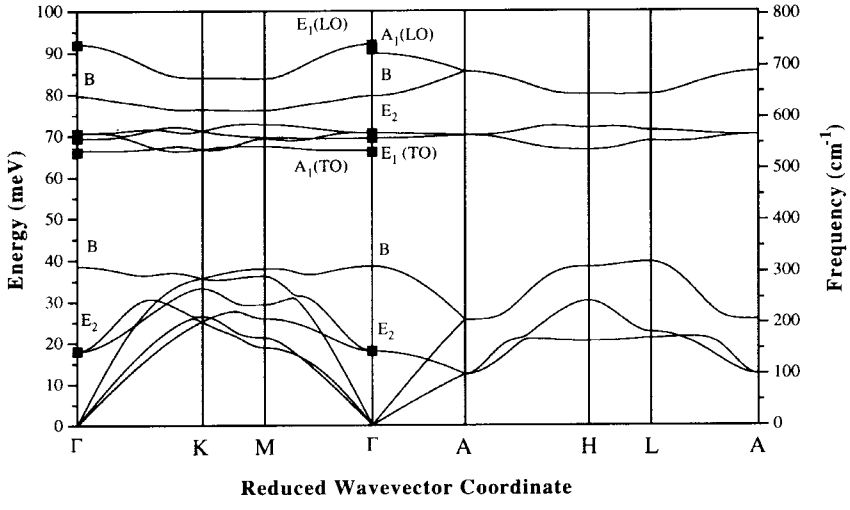

Figure 2: Calculated phonon dispersion curves of hexagonal GaN.

the spectrum taken from hexagonal GaN are the structures around 855cm^{-1}, 915cm^{-1} and 1000cm^{-1}. The 855cm^{-1} mode was not detected in cubic GaN. Considering the phonon dispersion curves and the fact that most of the structures are also found in the spectra taken from cubic samples, it becomes clear that only combinations between acoustic and optical phonons can provide the frequencies found. Because of the gap between the acoustic and optical phonon branches, which extends from 650-1100cm^{-1}, overtones can be excluded.

Most of the modes observed in the optical combination and overtone region (1100-1500cm^{-1}) were strongest in A_1 symmetry. The structure located at 1150cm^{-1} probably originates from the flatness of the dispersion curves in GaN in the energy region between the A_1(TO)=533cm^{-1} and E_2=569cm^{-1}. From the observed A_1 symmetry we infer a second-order process from the K- or the H-point in the Brillouin zone. As is the case in other hexagonal or cubic semiconductors the highest-frequency second-order Raman signal originates from optical-phonon overtones. In hexagonal GaN this region is dominated by two peaks at 1280cm^{-1} and 1313cm^{-1} and a camelback-like structure lying between 1340cm^{-1} and 1495cm^{-1} with maxima at 1385cm^{-1} and 1465cm^{-1}. Analogeous structures are found in cubic GaN. We will discuss in the follow-

ing these peaks starting with the structure highest in energy and proceeding toward lower energies. The highest-energy contribution of the second-order Raman signal with a cut-off at 1495cm^{-1} is attributed to an overtone of the zone-center E_1(LO) mode. Both, energy position and observed A_1+E_2 symmetry fits well together with theoretical predictions. The upper maximum of the camelback structure (1465cm^{-1}) corresponds to an overtone of the zone-center A_1(LO) mode. The lower camelback at 1385cm^{-1} together with its shoulder arises from the highest phonon branches which become flat at the zone boundary. Scattering processes originating from either the A-point, where the corresponding phonon branch runs extremely flat in direction to the H-point, or from the K-point are possible considering both energy and predicted symmetry. We found the camelback structure also in cubic GaN so a scattering process at the A-point can be excluded. The narrow peaks at 1280cm^{-1} and 1313cm^{-1} are extremely intense in A_1 symmetry but also weakly visible in E_1 symmetry. In E_2 symmetry the 1313cm^{-1} mode can also be seen but instead of the 1280cm^{-1} peak a weak mode appears at 1289cm^{-1}. Although combinations of the zone-center A_1(TO) and A_1(LO) modes and the corresponding E_1 modes are possible from energy considerations neither does the observed symmetry correspond to the expected symmetry nor can one explain their appearance in the cubic spectra. One possible explanation is that these modes are caused by combination processes at the zone boundary. On the other hand considering the phonon dispersion curves also an overtone-process of the B mode located around 640cm^{-1} is possible.

In conclusion, we have shown results from second-order Raman-scattering measurements on cubic and hexagonal GaN. We assigned most of the observed structures in the spectra to particular phonon branches and determined the points in the Brillouin zone from which the scattering originates. For this we have compared the energy positions and the symmetry behaviors of the modes with the selection rules derived by a group-theoretical analysis and the phonon dispersion curves.

References

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4. A detailed description of the second-order Raman-scattering selection rules in hexagonal GaN will be published.