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Raman Frequencies and Angular Dispersion of Polar Modes in Aluminum Nitride and Gallium Nitride

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We performed angular-resolved Raman-scattering experiments on AlN and GaN both grown in the wurtzite structure. Our measurements reveal that the transverse polar modes in AlN and GaN show a pronounced angular dispersion. We varied the angle between the phonon-propagation direction and the optical axis between 41° and 90° and observed a frequency shift of the $A_1(\text{TO})$ mode in the range of 28 cm^{-1} in AlN and of 15 cm^{-1} in GaN. The experimental values agree well with our theoretical calculations which were carried out using the DFT-LDA plane-wave pseudopotential method.

1. Introduction

The wide-bandgap semiconductors GaN and AlN are in the limelight of topical research due to their promising properties for optoelectronic applications in the blue to ultraviolet spectral range. Because of the huge lattice mismatch between usual substrates, e.g. sapphire or GaAs and the AlN and GaN layers there are difficulties in growing high-quality crystal layers [1]. The lattice mismatch causes a lot of defects near the substrate interface as well as in the layer. Here micro-Raman spectroscopy is an imperative tool for characterizing such structures. It provides information about strain, doping and local orientation with μm resolution both laterally and in the depth of a given sample as it is described e.g. by [2].

In uniaxial crystals the orientation of the optical axis plays an important role, when measuring phonon modes in Raman-scattering experiments. AlN and GaN normally crystallize in the hexagonal wurtzite structure (space group $C_{6v}^4\text{-P6}_3\text{mc}$) with four atoms in the unit cell. At the $\mathbf{k} = \mathbf{0}$ point group theory predicts the following eight sets of modes: $2A_1 + 2B + 2E_1 + 2E_2$ of which one A_1 , one E_1 , and two E_2 are Raman active. One set of A_1 and one of E_1 correspond to acoustic phonons. The B modes are silent [3]. Note that phonons with E_1 and E_2 symmetry, respectively, are twofold degenerate. The modes with A_1 and E_1 symmetry are also infrared active (i.e., they are polar modes) and therefore show an angular dispersion. This means that the energies of these

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modes depend on the direction of phonon propagation relative to the optical axis [4]. These modes are so-called quasi-TO and quasi-LO modes, respectively. The reason for this behavior of mode shifting lies in the anisotropy of the long-range Coulomb contributions (which correspond to the macroscopic field) in such uniaxial crystals and was described theoretically by Loudon [5].

When growing GaN on e.g. sapphire a tilting of the *c*-axis from its natural direction of growth is observed near the interface between the substrate and the crystal layer [2]. With micro-Raman spectroscopy it is possible to observe the tilting, and in combination with the knowledge of polar modes it enables us in principle to determine the amount of the tilting. To do so, information on the properties of the polar modes are required. Therefore we scrutinized the well-known law of Loudon for the two materials GaN and AlN both experimentally with Raman spectroscopy and theoretically with the help of *ab initio* calculations, and we were thus able to compare the experimental values with theoretical ones.

2. Technical Details of the *ab initio* Study

Our calculations were performed in the framework of the DFT-LDA plane-wave pseudopotential method. For the exchange-correlation energy the parametrization form of Perdew and Zunger [6] was used. For Al and N we generated soft norm-conserving pseudopotentials using a scheme proposed by Troulier and Martins [7]. The Brillouin-zone (BZ) integration of the wurtzite structure was carried out using twelve Chadi-Cohen special points [8]. The phonon frequencies at the $\mathbf{k} = \mathbf{0}$ point were determined within the framework of the self-consistent density-functional perturbation theory (DFPT) [9]. The dimension of the plane-wave basis set at a given \mathbf{q} point in the first BZ was fixed through the condition $\frac{1}{2}(\mathbf{q} + \mathbf{G})^2 \leq E_{\text{cut}}$, where \mathbf{G} is a reciprocal lattice vector and E_{cut} is the kinetic cutoff energy. For the calculation of the lattice dynamical properties at the equilibrium volume a value of 40 Ry for E_{cut} was used to ensure convergence of the calculated phonon frequencies within 3 cm^{-1} . Further computational details have been presented elsewhere [9, 10].

3. Experimental Methods

In order to compare the theoretical calculations of the angular dispersion with experiment we performed micro-Raman spectroscopy on AlN whisker crystals grown by direct reaction of aluminum vapor with nitrogen at high temperatures (1900 °C) and on a 200 μm thick GaN layer grown on sapphire by hydride vapor phase epitaxy (HVPE) at 1090 °C. Both materials were crystallized in the wurtzite structure. The Raman-scattering experiments were performed using a Dilor LABRAM single-grating spectrometer with a spectral resolution of about 1 cm^{-1} . The scattered light was detected by a charge-coupled device (CCD) detector with the help of confocal optical setup in which a super-notch filter suppressed light caused by Rayleigh scattering. To excite the Raman spectra the 632.8 nm line of a He–Ne laser was used. The excitation density was in the range of about 10^4 W/cm^2 ; reducing the excitation density on the sample surface by two orders of magnitude had no substantial effects on our measurements. The spectra were taken at room temperature either in backscattering geometry corresponding to $x(\cdot)\bar{x}$ configuration and in right-angle scattering geometry or $z(\cdot)\bar{x}$ configuration. It is com-

mon to call the z -axis the optical axis (c -axis). The other two axes are chosen arbitrarily but they form an orthogonal right-hand system with the c -axis. The direction of phonon propagation relative to the optical axis was determined in the following manner: We measured the angle of the incident laser beam and the scattered light relative to the crystal surface. From the conservation of wavevector $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_s$, where \mathbf{k}_i and \mathbf{k}_s describe the wavevector of the laser and the Stokes radiation, the direction could be determined. In order to change the direction of phonon propagation the crystals were rotated around the y -axis. In this way it was possible to determine the angle of the direction of phonon propagation with an accuracy of 2 to 8%. Because we changed the direction of incident and scattered light relative to the optical axis the difference between the ordinary and extraordinary refractive indices had to be considered when determining the angle between the direction of phonon propagation and the c -axis. However, within the accuracy of our measurement this distinction can be neglected. Due to the relatively high refractive indices in both materials [11] we did not succeed in measuring a noticeable mode shifting for small angles between the direction of phonon propagation and the c -axis.

4. Results and Discussion

We started with the computation of the structural parameters of AlN as a function of volume from *ab initio* total-energy calculations. For a given volume of the wurtzite unit cell, we optimized the structural degree of freedom a , c , and u and calculated the total energy. Then, we fitted the optimized total energies by the Vinet equation of state [12]. We obtained from the fitted equation of state the equilibrium volume V_0 , the lattice constants a and c , the internal parameter u , the bulk modulus B_0 , and the pressure derivative of the bulk modulus B'_0 (as shown in Table 1). The calculated structural parameters compare favorably with experiment, and are used for further investigation. Our theoretical results for the zone-center phonon frequencies are given in Table 2 and compared with the corresponding experimental data determined from the Raman spectra shown in Fig. 1. The energies of the single modes are in good agreement with the calculated frequencies to within about 10 cm^{-1} .

Table 1

Equilibrium lattice parameters a and c (in Å), internal parameter u , bulk modulus B_0 (in Mbar), the pressure derivative of the bulk modulus B'_0 , and tensors of the Born effective charge Z^B and of the dielectric constant ϵ_∞ in AlN

	a	c	u	B_0	B'_0	$(Z^B)_\perp$	$(Z^B)_\parallel$	$(\epsilon_\infty)_\parallel$	$(\epsilon_\infty)_\perp$
theor.	3.082	4.945	0.3821	2.15	3.63	2.696	2.696	4.618	4.379
expt. [19]	3.111	4.981	0.3816	2.08	6.30	2.573	2.573	4.680	4.680

Table 2

Comparison between theoretical and experimental Raman modes (in cm^{-1}) in AlN

	$E_2(\text{low})$	$A_1(\text{TO})$	$E_2(\text{high})$	$E_1(\text{TO})$	$A_1(\text{LO})$	$E_1(\text{LO})$
theor.	237	619	667	677	893	919
expt.	249	610	657	670	893 [15]	913

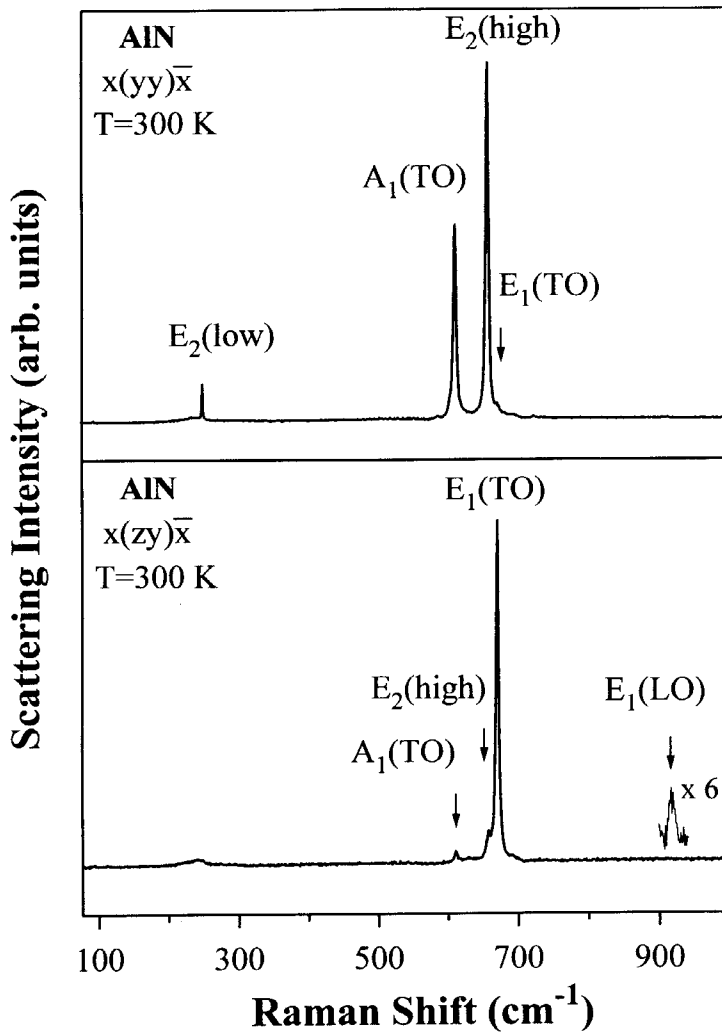


Fig. 1. Room-temperature Raman spectra of AlN taken in backscattering geometry for different polarizations

The experimental Raman spectra taken at room temperature in $x(yy)\bar{x}$ and $x(zy)\bar{x}$ geometry are plotted in Fig. 1. According to the selection rules for backscattering geometry [4], in the first spectrum the $A_1(\text{TO})$ mode appears at 610 cm^{-1} and the $E_2(\text{low})$ and the $E_2(\text{high})$ modes at 249 and 657 cm^{-1} , respectively. Considering the direction of phonon propagation [4] the $A_1(\text{LO})$ mode is not allowed in this scattering configuration. The second spectrum taken in E_1 symmetry shows only the $E_1(\text{TO})$ mode and the Fröhlich-allowed $E_1(\text{LO})$ mode at 670 and 913 cm^{-1} , respectively.

The calculated angular variation of the optical phonon frequencies of AlN is shown in Fig. 2. We found that the quasi-TO and quasi-LO modes exhibit a pronounced angular dependence and point out a stronger anisotropy of AlN than of the wurtzite structure of

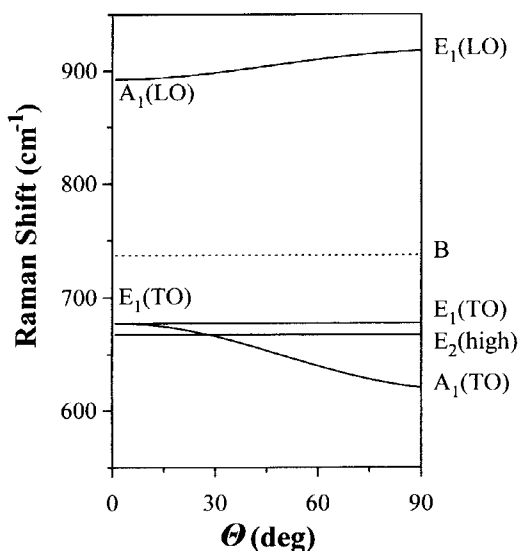


Fig. 2. Angular dependence of the optical modes of AlN. The angular-dependent (independent) modes are represented by solid (dotted) lines. Θ denotes the angle between the phonon wavevector and the c -axis

SiC [13]. The calculated frequency difference between the $A_1(\text{LO})$ and $E_1(\text{LO})$ ($A_1(\text{TO})$ and $E_1(\text{TO})$) modes is about 26 cm^{-1} (58 cm^{-1}) compared to the experimental value of 23 cm^{-1} [15] (60 cm^{-1}). For comparison, in the case of the wurtzite structure of SiC the experimental splitting between $A_1(\text{LO})$ and $E_1(\text{LO})$ and $A_1(\text{TO})$ and $E_1(\text{TO})$ amounts to 6.1 and 29.3 cm^{-1} [14].

Fig. 3a shows Raman spectra for different angles of the direction of phonon propagation relative to the c -axis taken in back-scattering geometry in AlN. One can see clearly that the $A_1(\text{TO})$ mode shifts by about 10 cm^{-1} to higher energies going from $\Theta = 90^\circ$ to 64° , where Θ denotes the angle between the direction of phonon propagation and the c -axis. Because the incident and detected polarization cannot be adjusted very precisely the $E_1(\text{TO})$ as well as the $E_2(\text{high})$ mode appear in all spectra. We point out that the $E_1(\text{TO})$ mode does not shift

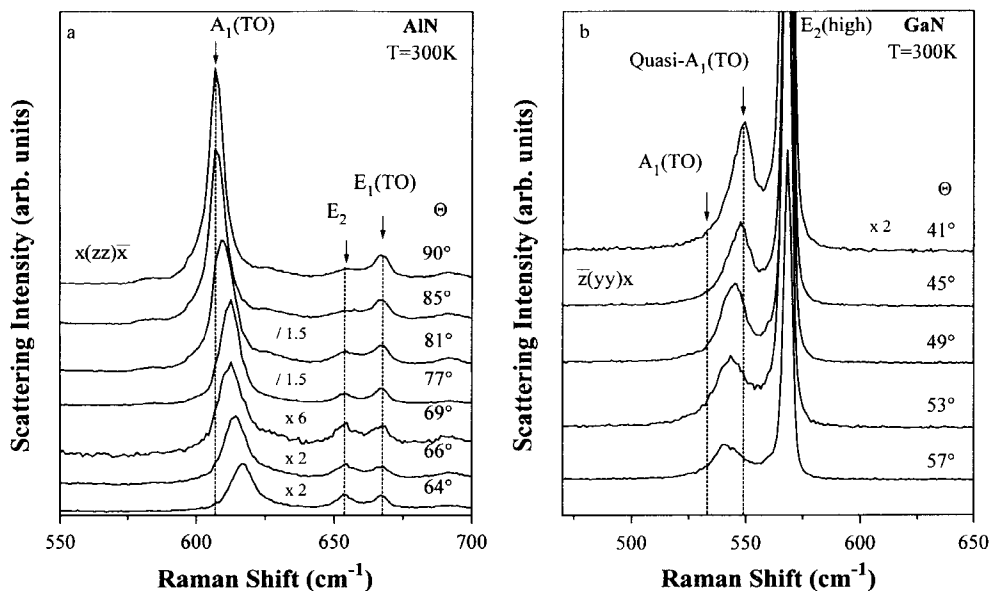


Fig. 3. Angular dependence of the $A_1(\text{TO})$ mode in a) AlN and in b) GaN for different directions of phonon propagation Θ relative to the c -axis. The spectra were taken at room temperature

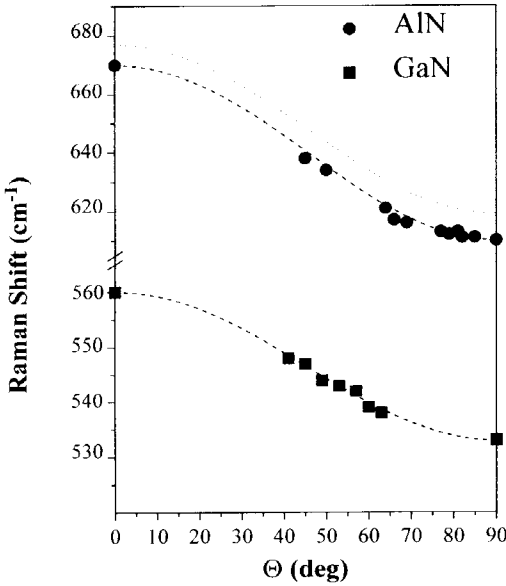


Fig. 4. Experimental data for the angular dependence of the $A_1(\text{TO})$ mode in AlN (solid circles) and in GaN (solid squares) for various directions of phonon propagation Θ relative to the c -axis. The dashed lines describe the angular dispersion of the quasi-TO modes calculated with equation (1). The dotted line represents the theoretical calculations of AlN

533 cm^{-1} , $A_1(\text{LO})$ mode at 735 cm^{-1} , $E_1(\text{TO})$ mode at 561 cm^{-1} , $E_1(\text{LO})$ mode at 742 cm^{-1} , and $E_2(\text{high})$ mode at 570 cm^{-1} . We also observed the $E_2(\text{low})$ mode at 145 cm^{-1} . Although the splitting between $A_1(\text{TO})$ and $E_1(\text{TO})$ is small compared to that of AlN, the shifting of the $A_1(\text{TO})$ mode can be observed. In Fig. 4 we present a plot of all measured frequencies of the quasi-TO modes in dependence of the phonon propagation direction in GaN and AlN. The dashed lines show the calculated frequency using the approximation given by Loudon [5]. The energies of the quasi-TO modes lie between the energy of the $A_1(\text{TO})$ and the $E_1(\text{TO})$ mode and fulfill the equation

$$\omega^2(\Theta) = [\omega_{E_1}(\text{TO}) \cos \Theta]^2 + [\omega_{A_1}(\text{TO}) \sin \Theta]^2, \quad (1)$$

in which $\omega(\Theta)$ denotes the frequency of the quasi-TO mode, $\omega_{E_1}(\text{TO})$ and $\omega_{A_1}(\text{TO})$ the frequency of the $E_1(\text{TO})$ and $A_1(\text{TO})$ mode, respectively. This approximation considers both the anisotropy of the force constant and the electrostatic forces associated with the vibrational modes and holds only for those crystals in which the frequency splitting between the LO and TO modes is much greater than the frequency splitting between the A_1 and E_1 modes (in AlN the TO–LO splitting of the A_1 modes is 279 cm^{-1} [15] versus the $A_1(\text{TO})$ – $E_1(\text{TO})$ splitting of 60 cm^{-1} ; in GaN the corresponding difference is 202 cm^{-1} versus 28 cm^{-1}). As can be seen from Fig. 4 the calculated angular dispersion of the $A_1(\text{TO})$ mode of AlN agrees well (apart from a constant shift of about 10 cm^{-1}) with the measured data. The DFPT calculations confirm also the validity of the Loudon approximation formula for the dispersion of the quasi-TO modes of both crystals. We remark that in spite of the small frequency splitting between the $A_1(\text{LO})$ and $E_1(\text{LO})$ modes a frequency shift of the $A_1(\text{LO})$ in AlN as well as in GaN was observed. For a phonon propagation direction of 45° relative to the c -axis the quasi-LO modes were obtained at 903 cm^{-1} in AlN and at 738 cm^{-1} in GaN. These values fit very well with the approximation by Loudon [5]; and also the frequency obtained by the DFPT method differs from the experimental value of 903 cm^{-1} only by 4 cm^{-1} .

The $A_1(\text{TO})-E_1(\text{TO})$ splitting can be also used as a measure of crystal anisotropy [14]. Another measure of anisotropy is the deviation of the c/a axial ratio from its ideal value $\sqrt{8/3}$. The axial ratio can in turn be related to the ionicity of the crystal [17]. The axial ratio of AlN and GaN, respectively deviates by $\Delta(c/a) = 0.032$ and 0.008 from the ideal value for hexagonal packing [18], and hence each lattice is distorted from the ideal geometry to some extent.

5. Conclusion

We have shown that the transverse polar modes in AlN and GaN exhibit a pronounced angular dispersion due to their structural anisotropy. We were able to observe quasi-modes in AlN and GaN for phonon propagation direction in an angular range of 41° to 90° relative to the optical axis. The experimentally determined energies of the quasi-TO modes follow the approximation given by Loudon [5] and agree also very well with our theoretical DFPT calculations for AlN. The anisotropy in the frequencies of the transverse optical phonons of the wurtzite structure of AlN and GaN is found to be larger than that of, e.g., the similar semiconductor SiC. Furthermore, we have shown that the frequency splitting of the transverse optical frequencies correlates with the structural anisotropy of the crystals given by the c/a axial ratios.

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