Raman spectra of folded acoustic phonons in short-period GaN/AlN superlattices as a tool for structure characterization

V Yu Davydov¹, E M Roginskii¹, Yu E Kitaev¹, A N Smirnov¹, I A Eliseyev¹, D V Nechaev¹, V N Jmerik¹ and M B Smirnov²

¹ Ioffe Institute, St. Petersburg, 194021, Russia
² St. Petersburg State University, Petrodvoretz, St. Petersburg, 194508, Russia

E-mail: Valery.Davydov@mail.ioffe.ru

Abstract. The results of experimental and theoretical studies of phonon modes in short-period GaN/AlN superlattices grown by PA MBE on the (0001) Al₂O₃ substrate are reported. In the framework of Density Functional Theory and Elastic Continuum Model the lattice dynamics properties are studied of (GaN)ₙ(AlN)ₘ SLs (ₙ₊ₘ≤24), where n and m are the number of monolayers. Good agreement between experiment and theory is found, which made it possible to establish unambiguously a relationship between the features observed in the Raman spectra and the microscopic nature of the acoustic phonon modes. The obtained results open new possibilities for analyzing the structural properties of GaN/AlN SLs by Raman spectroscopy.

1. Introduction
Wide band gap semiconductors GaN, AlN, and their alloys are a family of semiconductors that are crucial for modern optoelectronic devises operating in the middle ultraviolet spectral region, such as short-wavelength light emitting diodes, laser diodes, optical detectors etc., as well as for optoelectronic devices based on intersubband transitions and operating in infrared-terahertz spectral range [1]. Among the most important elements of such devices are short-period superlattices (SLs), the thickness of the component layers of which varies from one to several monolayers (ML). Quality control of grown samples is extremely important. The solution of these problems requires new methods of quantitative diagnostics of their parameters with atomic resolution. One such method may be Raman spectroscopy. Raman spectra measured in various scattering configurations give us data on phonon states whose frequencies depend on the structural parameters. Thus, by determining the phonon frequencies, one can obtain valuable information on the structure of the SL. In the case of a short-period SL, acoustic phonons are especially informative. A comprehensive review of acoustic phonons in arsenide-based SLs is given in [2]. Acoustic phonons in the nitride-based SLs were studied in [3,4]. This paper compliments these results by advancing the quantitative relationship between the frequencies of folded acoustic phonons and structural parameters such as the SL period and the layer thickness ratio.

2. Results and discussion

2.1. Experimental details
Short-period GaN/AlN SLs were grown on the c-plane AlN/sapphire using plasma-assisted molecular beam epitaxy (PA MBE) in a setup Compact 21T [5,6]. The digital epitaxy with short-term
interruptions of the Al-flux under a continuous Ga-flux, i.e. under Ga-rich growth conditions was used for SLs growth. The Ga excess over all GaN/AlN structures was evaporated by means of the post-growth annealing of the structures. The GaN$_m$/AlN$_n$ (m+n≤24) SLs, where m and n are the number of monolayers (MLs) in GaN quantum wells (QWs) and AlN barrier layers, respectively, were grown with equal (m=n) and different (m≠n) thicknesses. The total thickness of the structures varied from 0.6 to 0.8 μm. The high quality of GaN/AlN SLs was confirmed by high-resolution X-ray diffraction (XRD), high-resolution transmission electron microscopy, and Raman spectroscopy. Micro-Raman measurements were carried out at room temperature with a Horiba Jobin-Yvon T64000 triple spectrometer at the 532 nm excitation line.

2.2. Ab initio calculations

The ab initio calculations were carried out within local density approximation (LDA) to density functional theory (DFT) using the pseudopotential approach [7] as implemented in the ABINIT software package [8]. Dimension of the plane-wave basis set was limited by the energy cutoff of 45 Ha and the Brillouin zone (BZ) sampling according to the Monkhorst-Pack 6×6×4 scheme was used in calculations. Full geometry optimization was performed by varying both the parameters of the cell and the positions of atoms in the unit cell. The phonon wave vectors and frequencies were obtained in Γ-point of the BZ and Raman tensor components were calculated within the density functional perturbation theory (DFPT) [9]. All calculations were performed for infinite periodic SLs, thus impact of the limit SL length was not taken into account.

2.3. Group-theoretical analysis

When interpreting the Raman spectra in the low frequency spectral range (0–300 cm$^{-1}$), we can draw several important conclusions based only on the symmetry properties of SL with the P3m1 (#156) space group. The SL normal modes this spectral range are originated from the bulk longitudinal (LA) and transverse (TA) acoustic phonon branches $\Gamma_1 - A_1$ (LA) and $\Gamma_6 - A_6$ (TA) as well as from the optical $\Gamma_4 - A_4$ (silent) and $\Gamma_5 - A_5$ ($E_2$-low) ones. In the space group P6$_3$mc (#186) at the $A$-point of the BZ, the irreducible representations (irreps) form two pairs of conjugated irreps $A_1 + A_4$ and $A_5 + A_6$ which correspond to two degenerate phonon states each one combined from one acoustic and one optical phonon branch [10]. The formation of SLs lifts this degeneracy due to the lowering of space symmetry. As a result, the degenerate $A_1 + A_4$ state splits and transforms when folded into two $\Gamma_1$ ($A_1$) states with close frequencies. In turn the degenerate $A_5 + A_6$ state splits and transforms when folded into two $\Gamma_3$ ($E$) states also with close frequencies.

2.4 Folded LA modes

The group-theory analysis of the phonon symmetry in wurtzite-based (GaN)$_m$(AlN)$_n$ SLs leads to the conclusion that the folded LA phonons have $A_1$ symmetry and can be observed in $z(xx)\Sigma$ geometry (where $z$ is the direction of the $C_3$ optical axis). The Raman spectra of GaN/AlN SLs measured in the $z(xx)\Sigma$ scattering geometry in the low-frequency region of 50–300 cm$^{-1}$ are shown on the left side of figure 1. It can be seen that the spectra contain narrow lines whose positions vary depending on the SL period. Similar groups of lines also

![Figure 1](image-url)
exist in the calculated spectra shown on the right side of figure 1.

A good agreement between experiment and theory is found, which made it possible to establish unambiguously a relationship between the features observed in the Raman spectra and the displacement patterns of the acoustic phonon modes. An analysis of eigenvectors showed that these lines correspond to folded LA phonons with a wavelength equal to the SL period. The LA phonon line is also present in the spectra of non-equal constituent-layer-thickness SLs. Moreover, both in the experiment and calculations, it turned out that the positions of these lines depend not only on the total period but also on the ratio of the thicknesses of the constituent layers.

![Diagram](image)

Figure 2. (left panel) The low-frequency parts of the calculated $z(x)z$ Raman spectra for the 2×4 (a), 4×4 (b) and 6×4 (c) SLs. For each spectral peak, an atomic displacement pattern of the corresponding phonon mode is shown. Cation and anion displacements are shown by blue and red bars respectively. These are $x$-displacements for $E$-type modes (shown in red frames) and $z$-displacements for $A_1$-type modes (shown in blue frames). (right panel) SL layer deformations corresponding to LA-B (a) and LA-I (b) modes.

In figure 2 (left panel), the low-frequency parts of the calculated $z(x)z$ Raman spectra for 2×4, 4×4, and 6×6 SLs are shown. For the most noticeable spectral peaks, the atomic displacement patterns in the corresponding phonon mode are given. In the $A_1$-type modes (shown in blue frames), the atoms move along the $z$ axis, in the $E$-type modes (shown in red frames) the atoms move along the $x$ or $y$ axis. In the spectra shown, the LA-B mode lines have the highest intensity. These are longitudinal acoustic phonons with a wavelength equal to the SL period. The displacement patterns of these modes reveal that the largest displacement amplitudes correspond to atoms located on the interfaces with the atoms at neighboring interfaces oscillating in antiphase. Such a vibration corresponds to the uniform stress-strain of all SL layers followed by GaN layer expansion and AlN layer compression and vice versa (see figure 2 (right panel)). The frequency of this oscillation changes substantially with a change in the SL period. Close to the LA-B mode lines are the LA-I ones. According to the atomic displacement patterns shown in figure 2 (left panel), these modes are also LA phonons with a wavelength being equal to the SL period. However, the displacement patterns of these modes differ from the first ones: the largest amplitude displacements correspond to the atoms located in the middle of the layers, and the atoms located at the interfaces do not vibrate and remain fixed. In such an oscillation, one half of each layer contracts, the other stretches (see figure 2 (right panel)). It can be seen that in the LA-B mode, the changes in polarizability induced by deformations of neighboring layers are opposite in sign. Therefore, the total value of the derivative $\frac{\partial \alpha_{xx}}{\partial Q}$ will be proportional
to the difference $p_{13}(\text{GaN}) - p_{13}(\text{AlN})$. According to literature estimates, the values of the elasto-optical constants $p_{13}$ for GaN and AlN crystals differ by about 10% [11]. This difference is sufficient for the LA-B mode to have a significant activity in the Raman spectrum in the (xx)-polarization.

From the deformation map corresponding to the LA-I mode, one can understand why this mode has such a low Raman activity. In each layer, the changes in polarizability induced by the elasto-optical effect in the two halves of the layer have different signs and, therefore, cancel each other out. In the continuous medium approximation, the Raman intensity of this mode should be zero. The small, however non-zero value obtained in the calculation and in the experiment is due to the inadequacy of the continuum model, which is most significant in short-period SLs.

![Figure 3](image.png)

**Figure 3.** Dependence of the frequencies of the LA-B phonons on the inverse period length for several short-period GaN/AlN SLs according to the Raman spectroscopy data (a) and DFT calculations (b).

The continuum model also allows us to explain the observed frequency position of the LA-B line. If we express the frequency of this line depending on the inverse length of the SL period, we get the distribution shown in figure 3a (experiment) and in figure 3b (calculation). It can be seen that for equal constituent-layer-thickness SLs, both experimental and calculated frequencies fall on a straight line, the slope of which corresponds to the velocity of the longitudinal sound wave. The lines shown in figure 3 are constructed using the least square method. According to the slopes of these lines, the velocity $V_1$ in GaN/AlN SLs is 9356 m/s (experimental data) and 8694 m/s (calculation value), which is in a good agreement with the experimental value 9100 m/s [12] of the speed of sound in the $\text{Ga}_0.5\text{Al}_0.5\text{N}$ solid solution.

According to the continuous medium model [2], the velocity of a longitudinal sound wave in a binary SL with constituent layer thicknesses $d_1$ and $d_2$ is determined by the equation

$$V_{SL} = (d_1 + d_2) \left( \frac{d_1}{V_1} + \frac{d_2}{V_2} \right) = \left( \frac{1 - x}{V_1} + \frac{x}{V_2} \right)^{-1}, \quad x = \frac{d_2}{d_1 + d_2},$$

(1)

here $V_1$ and $V_2$ are the speeds of sound in bulk GaN and AlN crystals. For our case, we can take $V_1 = 8000$ m/s [13] and $V_2 = 11000$ m/s [14]. For equal constituent-layer-thickness SLs, Equation 1 reduces to

$$V_{SL} = \frac{(d_1 + d_2)}{V_1}, \quad 2 \left( \frac{1}{V_1} + \frac{1}{V_2} \right)^{-1} = 9260 \text{ m/s},$$

which practically coincides with the slope of the straight line in figure 3a.

Equation 1 allows us to estimate the dependence of the frequency of the quantized LA phonon not only on the SL total period but also on the ratio of the constituent layer thicknesses described by the composition parameter $x$. The $\omega(x)$ dependences determined from Equation 1 for two values of the SL period are shown in figure 4. It can be seen that the theoretical estimates obtained using Equation 1
correctly predict the sign of the slope of the $\omega(x)$ dependence but give approximately a half value of the slope. It can be assumed that such a discrepancy is due to neglect in Equation 1 of the effect of elastic stresses arising during the SL growth in the materials of the layers. Such stresses affect the elastic properties of materials, and their values depend on the ratio of constituent layer thicknesses.

2.5 Folded TA-modes

Figure 5 shows the experimental and calculated Raman spectra of equal constituent-layer-thickness GaN/AlN SLs for the $x(yz)\bar{x}$ scattering geometry. We see that in each such spectrum there are two low-frequency lines, indicated in figure 5 as 1 and 2. The group-theory analysis of the phonon symmetry in wurtzite-based (GaN)$_m$(AlN)$_n$ SLs leads to the conclusion that $E$ symmetry modes are active in the Raman spectra in the $x(yz)\bar{x}$ scattering geometry. In the low-frequency region of such spectra, the lines corresponding to the TA phonons should be observed. Both in the calculation and in the experiment, the frequency positions of lines 1 and 2 noticeably change depending on the period of the SL. The proximity of the positions of these peaks in the calculation and experiment and the similarity of their dependence on the structure allows us to suggest that lines 1 and 2 in the calculated and observed spectra correspond to the same phonons. To understand the nature of these modes, we turn to their eigenvectors obtained in calculations.

According to the calculation, two modes, TA-1 and TA-2, contribute to peak 1. The displacements of atoms in these modes are shown in figure 6. These displacements are directed perpendicular to the SL growth direction; thus, these modes are doubly degenerate. One can see that they correspond to the transverse acoustic waves with a wavelength equal to the SL period, that is, they can be identified as folded modes. The difference between the TA-1 and TA-2 is in the position of the nodal planes: in the TA-1 mode, they are located approximately in the middle of the layers, and in the TA-2 mode, they are approximately on the interfaces. The frequency difference between the TA-1 and TA-2 modes

![Figure 5. Raman spectra of the equal constituent-layer-thickness SLs measured in the $x(yz)\bar{x}$ geometry: experimental (a) and calculated (b).](image_url)
does not exceed 5 cm\(^{-1}\); therefore, such a splitting is impossible to notice in the experiment due to the finite line width. Two other acoustic modes, 2TA-1 and 2TA-2, contribute to peak 2. The corresponding patterns of atomic displacements are also shown in figure 6. It can be seen that these are the same standing acoustic waves, but with a wavelength equal to half the period of the SL. These are second-order confinement modes. The frequency difference between the 2TA-1 and 2TA-2 modes is slightly larger but still insufficient to notice their splitting in the experimental spectra.

| \(n \times m\) | TA-1 | TA-2 | 2TA-1 | 2TA-2 |
|----------------|------|------|-------|-------|
| 4×4            | ![Graph]( TA-1 4x4) | ![Graph]( TA-2 4x4) | ![Graph]( 2TA-1 4x4) | ![Graph]( 2TA-2 4x4) |
| 6×6            | ![Graph]( TA-1 6x6) | ![Graph]( TA-2 6x6) | ![Graph]( 2TA-1 6x6) | ![Graph]( 2TA-2 6x6) |
| 8×8            | ![Graph]( TA-1 8x8) | ![Graph]( TA-2 8x8) | ![Graph]( 2TA-1 8x8) | ![Graph]( 2TA-2 8x8) |

**Figure 6.** Atomic displacements in the TA and 2TA modes for several equi-period SLs.

As it was already noted [4], the frequency position of the TA and 2TA lines carries information that allows one to determine the period of the SL. In the elastic continuum approximation, the frequency of the acoustic TA and 2TA phonons is determined by the following relations:

\[
v(\text{TA}) = \frac{V_{\text{SL}}}{d}, \quad v(2\text{TA}) = 2\frac{V_{\text{SL}}}{d}
\]

where \(V_{\text{SL}}\) is the speed of sound in the SL, defined by the relation (1). For equal constituent-layer-thickness SLs, this expression can be simplified:

\[
V_{\text{SL}} = \frac{2V_1 V_2}{V_1 + V_2}
\]

The measured velocities of the TA[001] wave in GaN and AlN crystals are \(V_1 = 3.84 \text{ km/s}\) [13] and \(V_2 = 6.07 \text{ km/s}\) [14], respectively, which leads to an estimate of \(V_{\text{SL}} = 4.66 \text{ km/s}\). The dispersion relations corresponding to dependences (2) are shown by the solid lines in figure 7a. In this figure, experimental data and calculation results are shown. We can state a good agreement between the calculation and experiment. In addition, the result shows that even for very short-period SLs (4×4 ML), the dependence on the frequency period of the TA phonons is close to the linear one predicted by the elastic continuum model. For 2TA modes, this correlation is valid only for \(d \geq 12\) ML; for shorter periods, the frequency of the 2TA mode is noticeably lower than the value predicted by the elastic continuum approximation.

Figure 8a shows the Raman spectra of 5×7, 6×6, and 7×5 SLs. It can be seen that, according to calculations, the positions of peaks 1 and 2 change weakly with a change in the ratio of layer thicknesses. The same conclusion can be made with respect to peak 1 in the experiment, but peak 2 is difficult to identify in the experimental spectra. However, in the calculated spectra there is an additional peak (peak 3), the position of which shifts noticeably with a change in the ratio of layer thicknesses. Moreover, this peak shifts to the lower frequency with an increase in the AlN content: from 177 cm\(^{-1}\) in the 7×5 SL to 147 cm\(^{-1}\) in the 5×7 SL. Similar peaks can be seen in the experiment. It
is interesting to understand the nature of this peak and explain the observed shift. The calculated atomic displacements in the modes corresponding to peak 3 in the spectra are shown in figure 8d.

**Figure 7.** (a) Dispersion relations for the TA and 2TA phonons corresponding to the elastic continuum model (lines), experimental data (red circles) and the results of calculations (black squares). (b) Frequency dependence of the peak 3 on the AlN layer thickness: experimental data (red circles) and the results of calculation (black squares). The solid line corresponds to the dispersion of the TA-phonons in AlN. The dashed line shows the frequency of the $E_{2}$(low) phonon in GaN.

It can be seen that in this mode the atoms of the AlN layer predominantly oscillate, and the displacements of these atoms are close to those of the TA wave with a wavelength equal to the thickness of the AlN layer. It can be assumed that the frequency of such a mode should have a value close to what the dispersion relation for the TA phonons in AlN prescribes. As it was noted above, the transverse sound velocity in AlN in the [001] direction is 6.07 km/s. The corresponding linear dispersion is shown by the solid line in figure 7b. In the same figure, the symbols show the frequencies corresponding to peak 3 in the calculation and in the experiment. The data in figure 7b are in a good agreement with each other, but exceed the values predicted by the elastic continuum approximation by about 20 cm$^{-1}$.

This discrepancy increases as the frequency of these modes approaches the frequency of the $E_{2}$-low (GaN) mode. This effect indicates the mixing of two types of vibrations: a TA phonon localized in an AlN layer and an $E_{2}$ low phonon localized in a GaN layer. Such a mixing can be seen in figure 8d for the 5×7 SL.

**Figure 8.** Raman spectra of 5×7 (a), 6×6 (b) and 7×5 (c) SLs. The upper panels represent the experimental results, the lower ones show the result of calculations. (d) Atomic displacements in the modes corresponding to the peak 3.

3. Conclusion
In the low-frequency part of the spectra measured in the $z(xx)\bar{z}$ scattering geometry, the lines corresponding to the folded phonon modes $A_{1}(LA)$, in which atoms oscillate along the growth axis of the GaN/AlN SL, are detected. The lines are in the form of doublets. Their origin is due to the
presence of two types of folded LA phonons, which differ in the position of their nodal planes: in some modes, the nodal planes coincide with the interfaces, whereas in others they are located approximately in the middle of the layers. The Raman intensity of the modes of the first type (LA-I) is very small, since the contributions of the neighboring interfaces cancel each other out. The Raman intensity of the modes of the second type (LA-B) is noticeably higher, which is due to the difference in the values of the acousto-optical parameters of GaN and AlN. The dependence of their frequency position on the SL period is well described by a formula based on the elastic continuum model, which makes it possible to use these lines to estimate the SL period. We have shown that the frequency of the LA-B lines depends not only on the full period of the SL, but also on the ratio of layer thicknesses, which opens up new possibilities for the diagnosis of a multilayer structure.

In the low-frequency part of the spectra measured in the \textit{xyz} scattering geometry, there are lines corresponding to the folded E(TA) phonon modes, in which atoms oscillate in the directions perpendicular to the growth axis of the SL. In addition to the lines corresponding to the main folded TA modes, double-frequency lines are observed in the spectra that correspond to the TA modes with a doubled wave vector. The dependence of their frequencies on the SL period also correlates well with the predictions of the elastic continuum model. The possibility of observing the folded TA modes of the first and second order increases the reliability of the estimation of the period of SL obtained with their help. Besides the two lines corresponding to the folded TA modes, a small peak is observed in the range of 150–180 cm\(^{-1}\). Analysis of calculated eigenvectors made it possible to establish that this peak is associated with the TA phonon localized in the AlN layer. The presence of such modes in the studied SLs is due to the fact that the phonon branches of the TA phonons at the BZ boundary in GaN and AlN differ significantly. We have shown that the frequency of this line almost completely depends only on the thickness of the AlN layer, which opens up the possibility of using the detected dependence for a more detailed analysis of the SL structure.

References

[1] Beeler M, Trichas E and Monroy E 2013 \textit{Semicond. Sci. Technol.} \textbf{28} 074022
[2] Jusserand B and Cardona M 1989 
[3] Ibáñez J., Rapaport A, Boney C, Olivia R, CuscòR, Bensaoula A and Artús L 2012 \textit{J. Raman Spectroscopy} \textbf{43} 237–40
[4] Davydov V Yu, Roginskii E M, Smirnov A N, Kitaev Yu E, Yagovkina M A, Kyutt R N, Rozhavskaya M M, Zavarin E E, Lundin W V and Smirnov M B 2013 \textit{Phys. Status Solidi A} \textbf{210} 484–7
[5] Jmerik V N, Nechaev D V and Ivanov S V 2018 \textit{Molecular Beam Epitaxy (MBE): From Research to Mass Production, 2nd Edition}, ed. by M.Henini (Amsterdam: Elsevier) chapter 8 pp 135–79
[6] Nechaev D V, Koshelev O A, Ratnikov V V, Brunkov P N, Myasoedov A V, Sitnikova A A, Ivanov S V and Jmerik V N 2020 \textit{Superlattices and Microstructures} \textbf{138}, 106368
[7] Hamann D R 2013 \textit{Phys. Rev. B} \textbf{88} 085117
[8] Gonze X, Beuken J-M, Caracas R et al. 2002 \textit{Comput. Mater. Sci.} \textbf{25} 478–92
[9] Gonze X and Vigneron J-P 1989 \textit{Phys. Rev. B} \textbf{39} 13120–8
[10] Davydov V Yu, Kitaev Yu E, Goncharuk I N, Smirnov A N, Graul J, Semchinova O, Uffmann D, Smirnov M B, Mirgorodsky A P and Evarestov R A 1998 \textit{Phys. Rev. B} \textbf{58} 12899–907
[11] Davydov S Yu 2002 \textit{Semiconductors} \textbf{36} 41–4
[12] Deger C, Born E, Angerer H, Ambacher O, Stutzmann M, Hornsteiner J and Fischerauer G 1998 \textit{Appl. Phys. Lett.} \textbf{72} 2400–2
[13] Yamaguchi M, Yagi T, Azuhata T, Sota T, Suzuki K, Chichibu S and Nakamura S 1997 \textit{J. Phys.: Condens. Matter} \textbf{9} 241–8
[14] Kazan M, Moussaed E, Nader R and Masri P 2007 \textit{Phys. Status Solidi C} \textbf{4} 204–7