Phonons in short-period \((\text{GaN})_m(\text{AlN})_n\) superlattices: \textit{ab initio} calculations and group-theoretical analysis of modes and their genesis

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Abstract. The results of experimental and theoretical studies of phonon modes in short-period \((\text{GaN})_m(\text{AlN})_n\) superlattices (SLs) grown by MOVPE and PA MBE on the \((0001)\) \(\text{Al}_2\text{O}_3\) substrate are reported. Using a comprehensive group-theoretical analysis, the genesis of the SL vibrational modes from the modes of bulk AlN and GaN crystals has been established, which is important for interpreting the SL Raman spectrum. In the framework of Density Functional Theory, the lattice dynamics and the structural properties of \((\text{GaN})_m(\text{AlN})_n\) SLs \((m+n\leq12)\) were studied. An analysis of the eigenvectors of the phonon modes made it possible to reveal their microscopic nature. We established that the \(E\)\((\text{TO})\) modes are localized in the layers constituting the SL. It is shown that the localized nature of this mode is kept even in the SLs with the thinnest layers \((m+n=4)\). In turn, the \(A_1\)\((\text{TO})\) mode demonstrates a delocalized nature and reflects the averaged characteristics of the SL as a whole. A combined analysis of the \textit{ab initio} calculations and Raman data was performed. Thus, the above studies open new possibilities for analyzing the structural properties of GaN/AlN SLs by Raman and IR spectroscopy.

1. Introduction

The great interest of researchers, aimed at studying the physical properties of GaN/AlN superlattices (SLs), is due to their enormous potential for creating new generation devices with a wide range of applications. For example, short-period GaN/AlN superlattices can be used as a replacement for AlGaN solid solutions in the emitter layers of optoelectronic and electronic devices [1]. They can also be used to create unipolar devices operating on the basis of intersubband transitions in the near-IR range [2]. In addition, the ability to control elastic stresses in SLs allows them to be used as transition layers in structures with a strong lattice mismatch (for example, under growing structures on silicon substrates). From a fundamental point of view, short-period SLs can be considered as a metamaterial, simultaneously possessing both a number of properties inherent in ordinary solid solutions (effective band gap, average lattice parameter), and a number of completely new properties that are not fully studied at the moment.

The effective use of such periodic structures requires a detailed study of their fundamental physical properties, as well as the development of new quantitative diagnostics methods in order to improve their growth technology. Raman spectroscopy is a recognized tool for non-destructive study of the phonon spectrum of SLs with a high spatial resolution. Model methods for the study of phonon spectra form the basis for the quantitative analysis and interpretation of experimental information obtained by
vibrational spectroscopy. The existence of localized and delocalized modes in GaN/AlN SLs at frequencies different from the frequencies of any of the modes inherent in layers that comprise the SLs was predicted in theoretical studies carried out in the framework of the dielectric continuum model [3–5]. It was shown that phonons propagating in the direction of growth of the SL have a localized nature, while the phonons propagating in the perpendicular direction are delocalized ones. Joint analysis of theoretical and experimental results allows not only to more reliably interpret experimental results, but also provides a basis for developing a quantitative methodology for estimating important parameters of the studied SLs from the Raman spectroscopy data. However, to the best of our knowledge, only in two papers the results of ab initio calculations of the phonon modes GaN/AlN SLs are given, but they do not agree very well with the experimental data [6,7].

2. Results and discussion

2.1. Experimental details

GaN/AlN SLs were grown in a MOVPE system with a horizontal flow reactor at temperature of 1050°C on (0001) sapphire substrates using a double AlN–GaN buffer layer. The SLs period \( d_{SL} \) varied from 2 to 6 nm, and the thickness of the structures ranged from 0.3 to 1 \( \mu m \) [8]. GaN/AlN SLs were also grown by plasma-assisted molecular-beam epitaxy (PA MBE) on AlN/c-Al2O3 templates. The digital allowing epitaxy (DAE) with short-term interruptions of the Al-flux under a continuous Ga-flux, resulting in Ga-rich growth conditions was used for SLs growth. Excess Ga over all GaN/AlN structures was evaporated by means of the post-growth annealing of the structures. The period of the SLs grown by this technique also varied from 2 to 6 nm, and the thickness of the structures ranged from 0.3 to 0.6 \( \mu m \) [9]. 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. All spectra were measured in a backscattering geometry with \( z \) direction oriented along the \( c \)-axis of the SL.

2.2. Ab initio calculations

The ab initio calculations were carried out within local density approximation (LDA) to density functional theory (DFT) as realized in ABINIT software package [10–12]. In calculations we used the local density approximation (LDA). The norm-conserving pseudopotentials from [13] were used with the 3\( d \) electrons being considered as the valence ones. It was found that the convergence of total energy within 0.1 mHa was achieved with the energy cutoff of 45 Ha. The \( k \)-point grid was chosen according to the Monkhorst-Pack scheme [14] as \( 6 \times 6 \times 4 \). Full geometry optimization was performed by varying both the parameters of the cell and the positions of atoms in the unit cell. As a result, the internal pressure has been found to be less than \( 10^{-5} \) GPa. The phonon wave vectors and frequencies were obtained in \( \Gamma \)-point of the Brillouin zone within the density functional perturbation theory (DFPT) [15,16]. The Raman spectra were simulated from the Raman tensor calculated with perturbation theory, whose components are the third-order total-energy derivatives (with respect to the electric field and the atomic displacements). Applying the \((2n + 1)\) theorem, the Raman tensor can be found from the calculated first-order corrections to the wave functions of the ground state [17].

2.3. Group-theoretical analysis

In Ref. [18], the symmetry of (GaN)\(_m\)(AlN)\(_n\) superlattices was established to be described by two space groups depending on the number of atomic layers \((m+n)\) per primitive unit cell: \( C_{3V}^n \) (\( m+n \) is odd) and \( C_{3V}^n \) (\( m+n \) is even). In the SL family with \( C_{3V}^n \) symmetry, the primitive unit cell along the \( z \)-axis increases \((m+n)/2\) times and the number of atoms per primitive unit cells also increases \((m+n)/2\) times. The symmetry of normal modes at the Brillouin zone center is

\[ \Gamma_{ac} + \Gamma_{opt} = 2(m+n)(A_1 + E); \Gamma_{ac} = A_1 + E. \]

All optical modes are Raman-active and their number equals \( 4(m+n) - 2 \).
Table 1. Mode genesis in the SLs with \( m+n = 2k \) (C

\[3\]v).

| Phonons              | Optical | Acoustic* | Modes, observed in Raman spectra |
|----------------------|---------|-----------|---------------------------------|
| Bulk GaN и AlN      | \( A_1 \) | \( 2B_1 \) | \( E_1 \)                        | \( 2E_2 \) | \( A_1 \) | \( E_1 \) | \( A_1(\text{TO})+A_1(\text{LO})+2E_2 \) +\( E_{1(\text{TO})}+E_{1(\text{LO})} \) |
| (GaN)\(_1\)(AlN)\(_1\) | \( A_1 \) | \( 2A_1 \) | \( E \)                          | \( 2E \) | \( A_1 \) | \( E \) | \( 3[A_1(\text{TO})+A_1(\text{LO})+E(\text{TO})+E(\text{LO})] \) |
| (GaN)\(_2\)(AlN)\(_2\) | \( 2A_1 \) | \( 4A_1 \) | \( 2E \)                        | \( 4E \) | \( A_1(o)A_{1(a)} \) | \( E(o)E(a) \) | \( 7[A_1(\text{TO})+A_1(\text{LO})+E(\text{TO})+E(\text{LO})] \) |
| (GaN)\(_4\)(AlN)\(_4\) | \( 4A_1 \) | \( 8A_1 \) | \( 4E \)                        | \( 8E \) | \( 3A_1(o)A_{1(a)} \) | \( 3E(o)E(a) \) | \( 15[A_1(\text{TO})+A_1(\text{LO})+E(\text{TO})+E(\text{LO})] \) |
| (GaN)\(_6\)(AlN)\(_6\) | \( 6A_1 \) | \( 12A_1 \) | \( 6E \)                        | \( 12E \) | \( 5A_1(o)A_{1(a)} \) | \( 5E(o)E(a) \) | \( 23[A_1(\text{TO})+A_1(\text{LO})+E(\text{TO})+E(\text{LO})] \) |

*Indices (o) и (a) indicate optical and acoustic modes of SLs originated from acoustic modes of bulk crystals.

The genesis of the SL normal modes from the modes of bulk GaN and AlN crystals is very important for Raman spectra interpretation. In table 1, the sets of optical and acoustic modes originated from the bulk modes are given for 4 SLs with even \( m+n=2k \). It should be noted that SL optical modes originate both from optical and acoustic bulk modes.

Let us consider in detail the bulk mode transformation into SL modes. The \((\text{GaN})_1(\text{AlN})_1\) are obtained from the bulk GaN by substitution of one Ga atom in the primitive unit cell for Al. As a result, the number of acoustic modes does not change whereas their symmetry changes. In the frequency range of optical modes, the \( A_1 \) and \( B_1 \) bulk modes transform into the \( A_1 \) modes of SL \((\text{GaN})_1(\text{AlN})_1\). The number of the SL \( A_1 \) modes originated from the \( B_1 \) bulk modes is two times larger than the number of the SL \( A_1 \) modes originated from the \( A_1 \) bulk modes. Similarly, the number of the SL \( E \) modes originated from the \( E_2 \) bulk modes is two times larger than the number of the SL \( E \) modes originated from the \( E_1 \) bulk modes.

It can be seen that such a ratio is kept when increasing the SL period. In this case, the highest and the lowest branches originated from the successive splitting of branches will tend to the bulk GaN and AlN branches, respectively.

The optical \( A_1 \) modes of SLs originated from the acoustic \( A_1 \) bulk modes should be observed in the low frequency range of the SL Raman spectra. Their number equals \( [(m+n)/2 – 1] \). A similar situation takes place also for the \( E \) modes of SLs. In the SL family with the \( C_{3v} \) symmetry, all modes are IR-active and, as a result, have LO–TO splitting. Nevertheless, a pronounced LO–TO splitting can be expected only for the \( A_1 \) and \( E \) modes originated from the \( A_1 \) and \( E_1 \) bulk modes. Their number equals \((m+n)/2\) both for \( A_1 \) and \( E \) SL modes.

Based on the genesis of vibrational modes, one can make a conclusion on frequencies and intensities of the corresponding lines in the Raman spectra. Thus, we can predict that the \( A_1 \) modes originating from the \( B_1 \) silent modes will have Raman tensors with small components and will not be observed experimentally. The strongest \( A_1 \) Raman lines originate from the \( A_1 \) bulk modes. The number of these lines is equal to \((m+n)/2\). For example, in the \((\text{GaN})_4(\text{AlN})_4\) SLs, eight \( A_1 \) modes originating from the \( B_1 \) silent modes could not be experimentally observed. As a result, the strongest spectral lines predicted by theory are the \( 7A_1 \) and \( 7E \) ones, which agrees with the experiment.

3. Results and discussion
In order to verify the theoretical approach, the calculation of the structural and dynamical properties of wurtzite AlN and GaN single crystals was performed. The structural parameters, as well as the
calculated frequency values of vibrational modes in GaN and AlN single crystals at Γ-point of the BZ are found to be in a good agreement with experimental data [19,20].

After verification of the \textit{ab initio} approach, the calculations of structural parameters and frequencies of all phonon modes of the short-period (GaN)$_{m}$AlN$_{n}$ \((m=3,4,5)\) and (GaN)$_{m}$AlN$_{2m}$ \((m=5,6,7)\) SLs were performed. Here \(m\) is the number of GaN monolayers per SL unit cell. The calculated lattice parameters for SLs with equal thicknesses of constituent GaN and AlN layers \((m=n)\) as well as for those which thicknesses differ by one monolayer are presented in table 2 \((m\neq n)\). It can be concluded that the lattice parameters for SLs with \(m=n\) are close, which is not the case for SLs where the difference between \(m\) and \(n\) is quite large. The more AlN monolayers are contained in the SL period, the smaller the lattice parameters, and \textit{vice versa}. Such structural peculiarities should affect the dynamic properties. To estimate the relationship of local structural changes with the features of the phonon spectra, the frequencies and normal modes of the SLs at Γ-point of the BZ were obtained as eigenvalues and eigenvectors of the dynamical matrix calculated within DFPT.

\begin{table}[h]
\centering
\begin{tabular}{ccccccc}
\hline
 & (GaN)$_3$(AlN)$_2$ & (GaN)$_4$(AlN)$_3$ & (GaN)$_5$(AlN)$_4$ & (GaN)$_5$(AlN)$_7$ & (GaN)$_6$(AlN)$_6$ & (GaN)$_7$(AlN)$_3$ \\
\hline
\(a_h\), Å & 3.1084 & 3.1171 & 3.1258 & 3.1116 & 3.1174 & 3.1232 \\
\(c_h/N\), Å & 5.0158 & 5.0417 & 5.0671 & 5.0233 & 5.0406 & 5.0578 \\
\hline
\end{tabular}
\caption{Lattice parameters of the short-period GaN/AlN SLs.}
\end{table}

![Image](image-url)

\textbf{Figure 1.} Atomic displacements for the delocalized \(A_1\) mode \(\nu=576.4\text{cm}^{-1}\) \((a)\) of the \((\text{GaN})_4(\text{AlN})_4\) SL and Atomic displacements in the basal plane perpendicular to the \(c\)-axis for double degenerate mode \(E(\text{GaN})\) \(\nu=593.5\text{ cm}^{-1}\) \((b)\) localized in GaN layer of \((\text{GaN})_4(\text{AlN})_4\) and mode \(E(\text{AlN})\) \(\nu=643.0\text{ cm}^{-1}\) \((c)\) localized in AlN layer. Atomic displacements in two graphical representations: Blue, cyan and red circles denotes N, Ga and Al atoms correspondingly, arrows show directions of atomic displacements. Amplitudes of atomic displacements: blue, cyan and red bars correspond to the amplitudes of N, Ga and Al atoms, respectively.

The number and symmetry of normal modes in the calculated spectra are in complete agreement with the results of group-symmetry analysis. Examination of eigenvectors of the phonon modes led to the conclusion that there are mainly two types of phonon modes in the phonon spectra of short-period
GaN/AlN SLs. The modes of the first type are the delocalized ones. The $A_1$ mode ($\nu=576.4\text{ cm}^{-1}$) of the $(\text{GaN})_4(\text{AlN})_4$ SL genetically connected with $A_1$ mode of the bulk crystals is a good example of the delocalized one. The atomic displacement pattern of the $A_1$ mode is plotted in Figure 1 (a). This mode corresponds to the displacements of the anion sublattice with respect to the cation one in the opposite direction along the $c$ axis both in GaN and AlN layers. The modes of the second type are the localized modes. These modes involve the displacements of atoms only in GaN (or AlN) layers, while the atoms of the other AlN (or GaN) layers almost do not move. The analysis of calculated phonon spectra shows that the confinement of phonon modes is valid even for SLs with the thinnest layers ($m+n=4$). The $(\text{GaN})_4(\text{AlN})_4$ $E$ modes which are genetically connected with $E_1$ mode of the bulk crystal, are a good example of the localized ones. The atomic displacements of modes are plotted in Figures 1 (b,c).

The conclusion about the two types of modes inherent in the short-period GaN/AlN SLs is consistent with the results of earlier works [3–5].

In order to study the local structural changes by elucidating the relationships between the SL structure and SL phonon spectra, the Raman spectra of $(\text{GaN})_m(\text{AlN})_n (m=3,4,5)$ and $(\text{GaN})_m(\text{AlN})_{12-m} (m=5,6,7)$ SLs were calculated and the result of simulation is plotted in Figure 2. Additional comments are needed to explain the details of Raman spectra simulations for the localized modes. The scattering efficiency [9] could be expressed in the following equation:

$$\frac{ds}{d\Omega} = |\mathbf{e}_s \cdot \mathbf{R}_m \cdot \mathbf{e}_0|^2 = \frac{(\omega_m - \omega)^4}{c_1^2} |\mathbf{e}_s \cdot \mathbf{a}^m \cdot \mathbf{e}_0|^2 \cdot \frac{\hbar}{2\omega_m} \left( n(\omega_m) + 1 \right),$$

(1)

where $\Omega$ is the angle of collection in which the outgoing light is scattered, $\omega_m$ is the frequency of phonon involved in scattering process, $\mathbf{e}_0$ is the unit vector of incident light polarization with frequency $\omega_0$, $\mathbf{e}_s$ is the unit vector of scattered light polarization with frequency $(\omega_0 - \omega_m)$, $c_1$ is the light velocity in vacuum and $n(\omega_m)+1$ is the Bose-Einstein occupation number, $k_B$ is the Boltzmann constant, $T$ is the temperature (in K), and $\mathbf{d}^m$ is the Raman susceptibility tensor proportional to the derivative of the electronic linear dielectric susceptibility tensor $\chi^{(1)}_{ij}$ with respect to atomic displacements $r$ in mode $m$, which could be calculated within DFPT:

$$d_{ij}^m = \sqrt{\Omega_{ij}} \sum_{k,\beta} \frac{\partial \chi^{(1)}_{ij}}{\partial k_{\beta}} u_m(k\beta),$$

(3)

where $u_m$ are eigen displacements of atom $k$ along the direction $\beta$ in mode $m$.

As follows from equation (1), one have to take into account the influence of the angle of collection ($\Omega$) in which the outgoing light is scattered.

It was experimentally established in the present work, that the absolute intensity of the GaN $E_1$ bands is twice as much as the one of AlN. Thus scattering cross section for AlN is higher than the one of GaN. Such a large difference is significant in theoretical simulation of the intensity of confined Raman modes. Hence, in order to reproduce the experimental spectra, the intensities for $E$-symmetry modes confined in GaN layers were multiplied by factor 2.0.

It was found that the peaks positions and intensities are very close for the simulated Raman spectra of $(\text{GaN})_m(\text{AlN})_n$ and $(\text{GaN})_m(\text{AlN})_n$ SLs. In turn, in the Raman spectra of all $m\neq n$ SLs, drastic changes in the positions of both $A_1$ modes and $E$ modes should manifest themselves. Thus, calculations performed for $(\text{GaN})_m(\text{AlN})_{12-m}$ SLs ($m=3,5$) predict the delocalized $A_1$ line position shift either toward lower frequencies (~$10\text{ cm}^{-1}$) or higher frequencies (~$-9.5\text{ cm}^{-1}$) for $m=3$ and $m=5$, respectively. The calculations predict similar effects, though with smaller frequency shifts, also for delocalized mode in $(\text{GaN})_m(\text{AlN})_{12-m}$ SLs ($m=5,7$). For localized $E$ modes, strong frequency shifts occur with AlN thickness increase. Besides, the calculations show strong dependence of localized phonon intensity on thickness of layers forming the SL: the greater the layer thickness, the greater the Raman intensity of the phonon localized in this layer and vice versa the smaller the layer thickness, the lower the intensity (Figure 3 (a) and Figure 3 (c)).
Figure 2. (a,c) Calculated Raman spectra in the \(zz\)-polarization of the \(m=n\) and \(m\neq n\) SLs: (a) – \(d_{SL}=8\) ML; (c) – \(d_{SL}=12\) ML. (b,d) Experimental Raman spectra of GaN/AlN SLs with different period obtained in \(z(yz)\vec{x}\): (b) – \(d_{SL}=2\) nm (1 – \(d_{GaN}=1.3\) nm, \(d_{AlN}=0.7\) nm; 2 – \(d_{GaN}=1.0\) nm, \(d_{AlN}=1.0\) nm; 3 – \(d_{GaN}=0.7\) nm, \(d_{AlN}=1.3\) nm); (d) – \(d_{SL}=3\) nm (1 – \(d_{GaN}=1.7\) nm, \(d_{AlN}=1.3\) nm; 2 – \(d_{GaN}=1.5\) nm, \(d_{AlN}=1.5\) nm; 3 – \(d_{GaN}=1.3\) nm, \(d_{AlN}=1.7\) nm). Asterisks indicate lines of buffer layers. The insets show the theoretical calculations (solid lines) and experimental data (circles) for the phonon line \(A_1(\text{TO})\) (here, \(\vec{x} = n/(n + m)\)).

The baric behavior of the delocalized mode was studied by simulating uniaxial and biaxial strain applied to \((\text{GaN})_m(\text{AlN})_{8-m}\) SL. It was found that the frequency of the delocalized \(A_1(\text{TO})\) mode, in the case of uniaxial strain, increases with a slope of 0.45 cm\(^{-1}\)/Kbar, and decrease with a slope of 0.4 cm\(^{-1}\)/Kbar in the case of biaxial strain applied. Thus, one may assume that the mode is almost non sensitive to the strain in the SL. The conclusion about the delocalized nature of the \(A_1(\text{TO})\) mode is fully consistent with the results of the theoretical study of optical phonons in the short-period GaN/AlN SLs in the framework of the dielectric continuum model [4]. The conclusion about the weak effect of strain on the \(A_1(\text{TO})\) mode is also consistent with the results reported in Ref. [22], where, within the framework of the same model, it was shown that the elastic strain in SL layers caused by matching the GaN and AlN crystal lattice constants under a SL growth, has a weak effect on the delocalized mode frequency. However, in Ref. [7], where the phonons of short period SLs \((\text{GaN})_m(\text{AlN})_{8-m}\) with \(m=3,4,5\) were calculated using the DFT in the local-density approximation, the nature of the \(A_1\) mode was ascribed to mostly GaN-type. As a result, the variation in frequencies of this mode with the number of layers of AlN in SL was attributed to changes of the lattice constant \(a\) as well as the \(c/a\) ratio in SL.

Figures 2 (a) and 2 (c) show the results of simulation of the Raman spectra for the \(A_1(\text{TO})\) SL mode in \((\text{GaN})_m(\text{AlN})_{8-m}\) \((m = 3, 5)\) and \((\text{GaN})_m(\text{AlN})_{12-m}\) \((m = 5, 7)\) SLs, while Figures 2 (b) and 2 (d) show the experimental Raman spectra measured on these SLs. It can be seen that the calculated and measured spectra are in good qualitative agreement. The insets to the experimental spectra show the dependence of the frequency of the \(A_1(\text{TO})\) mode on the relative thickness of the AlN layer (\(\vec{x} = n/(m + n)\)) in the short-period GaN/AlN SLs proposed in Ref. [22]. The good agreement of the experimental data with this dependence, obtained for all the SLs studied, confirms the validity of the
theoretical predictions obtained in the present paper. Thus, the $A_1$(TO) mode should reflect the
averaged characteristics of the SL and the correlation dependence between the SL structure and the
frequency value of the delocalized polar phonon $A_1$(TO) can be used to quantify the Al(Ga)
concentration averaged over the GaN/AlN SL period. Combining this information with an estimation
of the total SL period obtained from the Raman spectra of the folded acoustic phonons [23], one can
determine the absolute values of the layer thicknesses of the multilayer structure.

Figure 3. (a,c) Calculated Raman spectra in the $yx$-polarization of the $m=n$ and $m\neq n$ SLs: (a) – $d_p=8$
ML; (c) – $d_{SL}=12$ ML. (b,d) Experimental Raman spectra of GaN/AlN SLs with different period
obtained in $z(yx)\bar{z}$: (b) – $d_{SL}=2$ nm ($d_{GaN}=1.3$ nm, $d_{AlN}=0.7$ nm; $2-d_{GaN}=1.0$ nm, $d_{AlN}=1.0$ nm;
3 – $d_{GaN}=0.7$ nm, $d_{AlN}=1.3$ nm); (d) – $d_{SL}=3$ nm ($1-d_{GaN}=1.7$ nm, $d_{AlN}=1.3$ nm; $2-d_{GaN}=1.5$ nm,
$d_{AlN}=1.5$ nm; 3 – $d_{GaN}=1.3$ nm, $d_{AlN}=1.7$ nm). Asterisks indicate lines of buffer layers.

The baric behavior of the localized modes was also studied by simulating uniaxial and biaxial
strain applied to (GaN)$_m$(AlN)$_n$ SL. It has been found that the $E$(TO) mode is very sensitive to the
biaxial strain. Calculations show that the frequencies of the modes localized in the GaN layers turn out
to be higher, and those of the modes localized in the AlN layer turn out to be lower than their values in
bulk GaN and AlN crystals. From this we can conclude that the GaN layers forming the SL are
compressed in the plane whereas the AlN layers are stretched in the plane. This conclusion is in good
agreement with the results of [4,7]. Figures 3 (a) and 3 (c) show the results of the simulated Raman
spectra for the $E$(TO) mode for (GaN)$_m$(AlN)$_n$ SLs, respectively. Figures 3 (b) and 3 (d) show the expe rimental Raman spectra measured on such SLs. It
can be seen that the calculated and measured spectra are in good qualitative agreement. Thus, the
positions of lines in Raman spectra corresponding to the localized modes can be used to quantify the
magnitude of strain in the individual layers forming the SL.

4. Conclusion
Experimental Raman spectra were obtained for short-period GaN/AlN SLs grown by MOVPE and PA
MBE on the (0001) Al$_2$O$_3$ substrate. A comprehensive group-theoretical analysis made it possible to
establish the genesis of the SL phonon modes from the modes of bulk AlN and GaN crystals. Based on
the genesis of the phonon modes, the conclusions on the frequencies and intensities of the corresponding lines in the Raman spectra of the SL have been made. The lattice dynamics and structural properties of the (AlN)\textit{m}(GaN)\textit{n} SLs (\textit{m}+\textit{n} \leq 12) have been studied by \textit{ab initio} calculations within the framework of the density functional theory. As a result, the phonon mode frequencies were calculated and the atomic displacement pattern was established. The number and symmetry of vibrational modes in the calculated spectrum in complete agreement with the results of the group-theoretical analysis. This led to the conclusion on the microscopic nature of the vibrational modes of the SL.

It has been established that the \textit{E}(TO) modes are localized in the constituent SL layers and can be used to obtain information about the individual characteristics of each layer forming the SL. It is shown that the localized nature of the mode of this symmetry is preserved even in the SL with the thinnest constituent layers, i.e. for \textit{m}+\textit{n}=4. In turn, the \textit{A}\textsubscript{1}(TO) mode has a delocalized nature. This allows one to use the parameters of this mode to estimate the averaged characteristics of the SL as a whole. On the basis of the Raman susceptibility tensor, the theoretical Raman spectra were calculated and compared with experimental ones. The results of the \textit{ab initio} calculations are in a good agreement with the experimental Raman data. The correlation dependencies between the SL structure and the frequencies of the localized and delocalized polar phonons were obtained. Hence, the results of the above studies form the basis for the quantitative estimation of both strain in individual layers forming the SL and the Al(Ga) content averaged over the SL period. They also open new possibilities for analyzing other important parameters of short-period GaN/AlN SLs.

References

[1] Munoz E, Monroy E, Pau JL, Calle F, Omnes F, Gibart P 2001 \textit{J. Physics: Cond. Matter} \textbf{13} 7115
[2] Beeler M, Trichas E and Monroy E 2013 \textit{Semicond. Sci. Technol.} \textbf{28} 074022
[3] Gleize J, Renucci M A, Frandon J and Demangeot F 1999 \textit{Phys. Rev. B} \textbf{60} 15985
[4] Smirnov M B, Karpov S V, Davydov V Yu, Smirnov A N, Zavarin E E and Lundin V V 2005 \textit{Physics of the Solid State} \textbf{47} 716
[5] Zhang L 2011 \textit{Phys. Status Solidi C} \textbf{248} 2120
[6] Wagner J-M and Bechstedt F 2000 \textit{Int. Conf. on Phys. of Semicond., ICPS-25}, Osaka
[7] Paudel T R and Lambrecht W R L 2009 \textit{Phys. Rev. B} \textbf{80} 104202
[8] Lundin W V, Sakharov A V, Tsatsulnikov A F and Ustinov V M 2011 \textit{Semicond. Sci. Technol.} \textbf{26} 014039
[9] Jmerik V N, Nechaev D V and Ivanov S V 2018 Molecular Beam Epitaxy (MBE): From \textit{Research to Mass Production, 2nd Edition}, ed. by M.Henini, (Amsterdam: Elsevier) chapter 8 pp 135–179
[10] Gonze X, Beuken J-M, Caracas R et al. 2002 \textit{Comput. Mater. Sci.} \textbf{25} 478
[11] Gonze X, Rignanese G, Verstraete M et al. 2005 \textit{Z. Kristallogr.} \textbf{220} 558
[12] Gonze X, Amadon B, Anglade P-M et al. 2009 \textit{Comput. Phys. Commun.} \textbf{180} 2582
[13] Hamann D R 2013 \textit{Phys. Rev. B} \textbf{88} 085117
[14] Monkhorst H J and Pack J D 1976 \textit{Phys. Rev. B} \textbf{13} 5188
[15] Gonze X 1997 \textit{Phys. Rev. B} \textbf{55} 10337
[16] Gonze X and Lee C 1997 \textit{Phys. Rev. B} \textbf{55} 10355
[17] Gonze X and Vigneron J-P 1989 \textit{Phys. Rev. B} \textbf{39} 13120
[18] Kitaev Yu E, Limonov M F, Tronc P and Yushin G N 1998 \textit{Phys. Rev. B} \textbf{57} 14209
[19] Schulz H and Thiemann K H 1977 \textit{Solid State Comm.} \textbf{23} 815
[20] Davydov V Yu, Kitaev Yu E, Goncharuk J 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
[21] Veithen M, Gonze X and Ghosez Ph 2005 \textit{Phys. Rev. B} \textbf{71}, 125107
[22] Pankin D V, Smirnov M B, Davydov V Yu, Smirnov A N, Zavarin E E and Lundin W V 2016 \textit{Semiconductors} \textbf{50} 1043
[23] Davydov V Yu, Roginski 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