

# Influence of AlN/GaN superlattice period on frequency of polar optical modes

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**Abstract.** Polar optical phonons in the binary AlN/GaN superlattices (SL) were studied in the framework of dielectric continuum model (DCM). It is shown that the modes propagating in the interface plane are delocalized over all layers and the modes propagating along the SL axis are delocalized in certain layers. Frequencies of former strongly depend on the layer thickness ratio and frequencies of the latter do not depend on the SL structure. Such behavior is typical for the short-period SL. We show that a strong coupling between two types of the modes takes place at increasing SL period. The phenomenon is described mathematically by the frequency-structure relations and its physical meaning is discussed.

## 1. Introduction

The nanostructures based on the A<sup>III</sup>N nitrides attract much attention owing their great potentiality for modern optoelectronics. Particularly, the AlN/GaN superlattices (SL) are used as active material in various devices operating in ultraviolet and infrared spectral regions. They are used as a key element in deep-ultraviolet light emitting diodes and in high-speed infrared intersubband optical devices such as intensity modulators, optically pumped light emitters, and photodetectors [1, 2]. Due to great importance of these systems for applications, the structure control of the grown SL is an imperative issue. Raman spectroscopy is a rather efficient technique for a fast nondestructive sample characterization. It was found that some of the Raman-active phonon modes are rather sensitive to particularities of the SL's structure: frequencies of the delocalized polar modes with wave vectors parallel to the interface plane strongly depend on the layer thickness ratio [3]. This phenomenon is due to the strong long-range dipole-dipole interactions and is specific feature of the nitride-based SLs.

Strong correlations between phonon frequencies and SL's structure opens possibility to use Raman spectroscopy for the structure characterization. In this connection it is important to established precise quantitative relations between phonon frequencies and structural parameters. Structure of a binary SL is described by thickness of the constituent layers  $d_1$  and  $d_2$  (here and below we use '1' for GaN and '2' for AlN) or alternatively by total period  $d=d_1+d_2$  and the layer thickness ratio  $f=d_1/(d_2+d_1)$ . Another key parameter for the Raman scattering process is the wavelength of the scattered light whose wave length  $\lambda$  customary is about 500 nm. Depending on the  $d$  value all studied SL can be divided in two groups: the short-period SLs ( $d \ll \lambda$ ) and long-period SLs ( $d \sim \lambda$ ). Most attention was paid to the short-period SL owing their great potentiality for the optoelectronic applications [4]. The long-period SL also attract some interests due to their applications in the distributed Bragg reflectors [5] and in the ultraviolet light-emitting diodes [6]. First thorough discussion of the phonon-structure relations was focused on the dependence of the phonon frequencies on the SL period, or rather on the ratio  $d/\lambda$ .



referred as  $s$ -parameter [7]. Later, dependence of the phonon frequencies on the layer thickness ratio (i.e. on the  $f$ -parameter) also was considered [3]. However, this analysis dealt only with the short-period SL (for  $s \ll 1$ ). A complex analysis which considered both these impacts was not done. This study is aimed to fill this gap.

## 2. Method

The long-range dipole-dipole interactions can be taken into account in the frame of the dielectric continuum model (DCM) [8]. Such approach does not deal with atomistic structure of the materials and consider SL as sandwich-like infinite periodic solid matter. Dielectric matrix is periodic function which takes in any layer the values of corresponding constituent crystals. Both AlN and GaN are hexagonal wurtzite-like crystals, and the AlN/GaN SL grows along the hexagonal axes. Thus, the SL is a uniaxial system and dielectric constant matrix has the form

$$\boldsymbol{\varepsilon} = \begin{pmatrix} \varepsilon_{xx} & & \\ & \varepsilon_{xx} & \\ & & \varepsilon_{zz} \end{pmatrix} \quad (1)$$

in all layers. Polar phonon modes in the short-period nitride-based SL can be divided into A and E symmetry representations [7,9]. The A-modes are polarized along the  $z$ -axis (axis of structure growth), and E-modes are polarized in the perpendicular direction (in the  $xy$ -plane corresponding to the interface plane). Hence the phonon contributions to the dielectric function can be written as follows [10]:

$$\varepsilon_{xx}(\omega) = \varepsilon^\infty \frac{\omega_{E(\text{LO})}^2 - \omega^2}{\omega_{E(\text{TO})}^2 - \omega^2}, \quad \varepsilon_{zz}(\omega) = \varepsilon^\infty \frac{\omega_{A(\text{LO})}^2 - \omega^2}{\omega_{A(\text{TO})}^2 - \omega^2} \quad (2)$$

Dielectric parameters for AlN and GaN crystals are listed in Table 1.

**Table 1.** Dielectric parameters for AlN and GaN crystals.

	Unit	AlN	GaN
$\omega_{A(\text{TO})}$	$\text{cm}^{-1}$	610 [11]	531 [18]
$\omega_{E(\text{TO})}$	$\text{cm}^{-1}$	669 [11]	559 [18]
$\omega_{A(\text{LO})}$	$\text{cm}^{-1}$	890 [11]	734 [18]
$\omega_{E(\text{LO})}$	$\text{cm}^{-1}$	911 [11]	742 [18]
$\varepsilon^\infty$		4.84 [13]	5.35 [14]

Essence of the DCM approach is solving the Maxwell equations

$$\text{rot} \mathbf{E} = 0, \quad \text{div} \boldsymbol{\varepsilon} \mathbf{E} = 0 \quad (3)$$

for the plane-wave field

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_0 \exp(i\mathbf{q}\mathbf{r}) \quad (4)$$

and the frequency dependent dielectric matrix (1-2).

The  $z$ -axis is directed along the periodicity direction,  $x$  and  $y$ -axes lay in the interface plane. We consider the waves with wave vector  $\mathbf{q}$  directed along the  $x$ -axis. Hence, the electric field components can be written as

$$E_x = E_x(z) \exp(iqx), \quad E_y = 0, \quad E_z = E_z(z) \exp(iqx). \quad (5)$$

Using the equations (3) one obtains

$$\frac{d}{dz} E_x(z) - iqE_z(z) = 0, \quad iq\varepsilon_{xx}E_x(z) + \varepsilon_{zz} \frac{d}{dz} E_z(z) = 0. \quad (6)$$

Solutions of these linear differential equations can be found by substituting  $E_x(z) = E_x^0 \exp(gz)$  and  $E_z(z) = E_z^0 \exp(gz)$ . This leads to the relations:

$$gE_x^0 - iqE_z^0 = 0, \quad iq\epsilon_{xx}E_x^0 + g\epsilon_{zz}E_z^0 = 0 \tag{7}$$

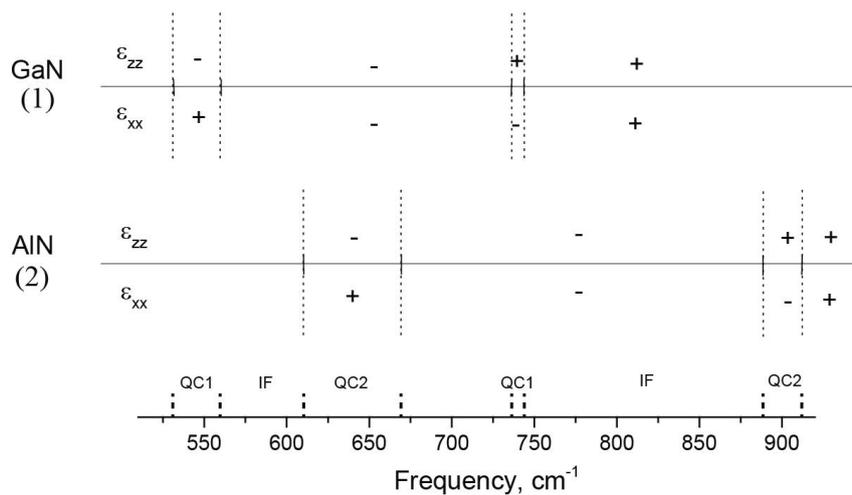
from which one can conclude:

$$-q^2\epsilon_{xx} + g^2\epsilon_{zz} = 0. \tag{8}$$

Using equation (8) one can determine  $g$ -index for any given  $q$ -index. Recall the latter defines wavelength of oscillations along  $x$ -direction and the former describe exponential decay along  $z$ -axis. Value of the  $g$ -index depends on the dielectric constant ratio:

$$g = \pm q \sqrt{\frac{\epsilon_{xx}}{\epsilon_{zz}}} = \pm qr \tag{9}$$

Recall that in the DCM approach the dielectric constants are frequency-dependent and can take positive or negative values. Thus, depending on sign of the  $\epsilon_{xx}/\epsilon_{zz}$  ratio  $g$  can be real or imaginary. The first type of solutions corresponds to the exponential decay  $z$ -dependence, and the second one is related to the oscillatory  $z$ -dependence. On analyzing the  $\epsilon_{xx}$  and  $\epsilon_{zz}$  values for the GaN and AlN crystals in the wide frequency interval one can determine the frequency regions in which different types of DCM solutions are expected.



**Figure 1.** Frequency dependence of sign of the  $\epsilon_{xx}/\epsilon_{zz}$  ratio for AlN and GaN crystals.

One can see that there are two intervals in which the  $\epsilon_{xx}/\epsilon_{zz}$  ratios are positive for both crystals. They correspond to the so-called interface (IF) phonons. Besides there are intervals in which the  $\epsilon_{xx}/\epsilon_{zz}$  ratio is positive for one crystal and negative for another. They correspond to the so-called quasi-confined (QC) phonons which have oscillatory character in one material and the exponential decay character in another. We shall discriminate them by index ‘1’ (oscillations in GaN) and ‘2’ (oscillations in AlN). Solutions of equations (8-9) for all the layers 1 (GaN) and 2 (AlN) must be supplemented by the boundary conditions:

$$E_{1,x} = E_{2,x}, \quad \epsilon_{zz}^1 E_{1,z} = \epsilon_{zz}^2 E_{2,z} \tag{10}$$

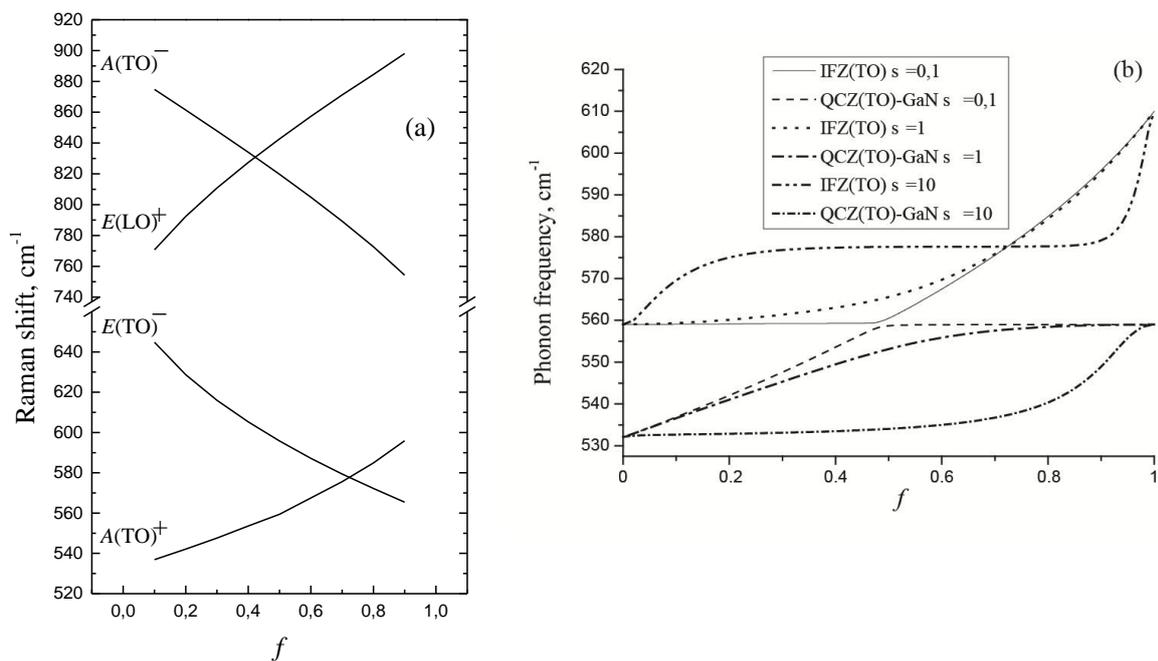
The considered SL structure is symmetric with respect to plane passing through the middle of any layer. Hence, all solutions must be invariant or anti-invariant with respect to the mirror-plane transformation. Besides, the solution invariant with respect to  $E_x$  must be anti-invariant with respect to  $E_z$  and vice versa (see equation 6). We shall refer the solutions invariant with respect to  $E_z$  as IFZ and QCZ, and the solutions invariant with respect to  $E_x$  as IFX and QCX.

Summarizing, the phonon frequency region can be divided in six intervals (see figure 1). Within every interval, the DCM allows determining two phonon states: either IFZ and IFX, or QCZ and QCX. Frequencies of all phonons depend on two structural parameters: the total period described by dimensionless parameter  $s=q(d_1+d_2)$  and the layer thickness ratio which we shall characterize by parameter  $f=d_1/(d_2+d_1)$ .

It was shown that these dependencies can be easily established for the short-period SL, i.e. in the  $s \rightarrow 0$  limit. In this case one can assume  $q=0$  and  $g=0$ . This means that the electric fields are homogeneous in all layers, the quasi-confined (QCX and QCZ) modes are fully confined in the certain layers, and the IFZ and IFX modes are delocalized over all layers. Moreover, in the  $s \rightarrow 0$  limit, all modes are strongly polarized: the solutions IFZ and QCZ correspond to  $E_x=0$ , and the solutions IFX and QCX correspond to  $E_z=0$ .

Evidently, frequencies of the completely confined QCX and QCZ modes correspond to corresponding parameters of the constituent bulk material. Frequencies of the completely delocalized IFX and IFZ modes can be determined by simple calculations based on the equations (2, 10). These frequencies  $\omega$  depend on the layer ratio parameter  $f$  as it is shown in figure 2. Now we turn to the central question – how do these dependencies change along with increasing  $s$  value?

Analytic equations for solving this problem were presented in [7]. Solving these equations with various  $s$  and  $f$  values we have calculated. The results are shown in figure 2(b) as three sets of the  $\omega(f)$  dependencies corresponding the for  $s=0.1, 1, 10$ . In this paper we focus our attention on the frequency of  $A_1(\text{TO})$ -mode.



**Figure 2.** Frequencies of polar modes of  $(\text{GaN})_m(\text{AlN})_n$  in dependence on the layer thickness parameter  $f$ . (a):  $s=0$  (b): IFZ(TO) and QCZ(TO)-GaN modes at different  $s$  values.

### 3. Discussion

In the case of  $s=0.1$  it is seen that IFZ(TO) and QCZ(TO)-GaN smoothly merge together at  $\omega=\omega_{E(TO)1}$  forming the curve which is very close to that representing the dependence for the  $A(TO)^+$  (or  $A_1(TO)$ ) mode in figure 2a (i.e. in the  $s = 0$  limit).

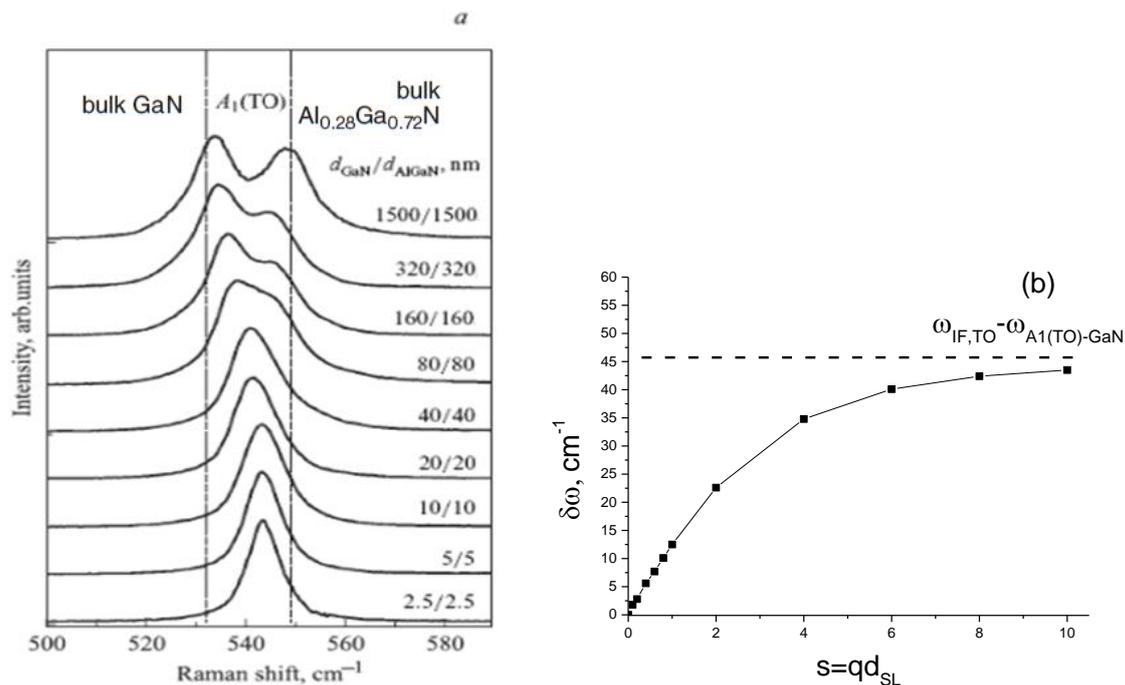
In the case of  $s = 1$  the curves have no common points: they diverge on approaching to the line  $\omega = \omega_{E(TO)1}$ . Such behaviour indicates a strong coupling between IFZ(TO) and QCZ(TO)-GaN modes. The latter is no longer confined at  $s \neq 0$ . The nature of this coupling is quite evident: at finite wave vector directed along interface plane the atomic oscillations in  $z$  and  $x$  directions are dynamically coupled. The dependencies presented in figure 2b show that at  $f < 0.47$  QCZ(TO)-GaN curve at  $s=1$  deviates from that at  $s=0.1$  not far than  $8 \text{ cm}^{-1}$ . The same is true in respect IFZ(TO) curves at  $s=1$  and  $s=0.1$  at  $f > 0.47$ . This allows an estimation of accuracy of the long wave approximation as  $8 \text{ cm}^{-1}$  at  $s < 1$ .

At thicker layers, divergence of the QCZ(TO)-GaN and IFZ(TO) curves becomes more considerable. This is illustrated by calculation at  $s=10$ . This evidences essential difference between IF and QC modes in a long- period SL. At  $s=10$  the curves exhibit a large plateau in the large interval  $0.2 < f < 0.8$ . Physically, this means that frequencies of these modes do not depend on the layer thickness. Frequencies of QCZ(TO)-GaN modes take the values of the bulk  $A(TO)$ -GaN phonons, and frequency of the IFZ(TO) mode takes the value of  $\omega_{IF(TO)}=578.5 \text{ cm}^{-1}$ . Note, that this value exactly corresponds to the IF mode localized on the single free-standing heterojunction [15].

The structure related phonon mode splitting can be illustrated by experimental data reported in [3]. Raman spectra of the GaN/Ga<sub>0.28</sub>Al<sub>0.72</sub>N SLs with  $d_1 = d_2$  and with  $d$  varying from 2.5 up to 1500 nm are shown in figure 9. They clearly manifest that at increasing  $d$  the following transformations occur: the single intense line corresponding to IFZ mode is clearly seen in the spectrum of the short-period SLs (up to  $s = 1$ ); then it becomes to enlarge and at  $s \approx 10$  evidently splits into two components which gradually diverge and at  $s \approx 100$  achieve the frequencies typical for  $A(TO)$  modes in bulk crystals. This phenomenon is in line with the transformations shown in figure 2b: the single line observed in short period SL (curves IFZ(TO) and QCZ(TO)-GaN at  $s=0.1$ ) splits in a doublet (curves IFZ(TO) and QCZ(TO)-GaN at  $s=1$ ) at intermediate  $s$  values, and the two spectral lines can be observed in the long-period SLs (curves IFZ(TO) and QCZ(TO)-GaN at  $s=10$ ). The calculated splitting value is shown in figure 3b.

### 4. Conclusions

It was found that magnitude of frequency splitting between two  $A_1(TO)$  phonon components in the equi-thick AlN/GaN SL depends on SL period. It is equal to zero in the case of short-period SL and reaches maximal value in the case of long-period SL (the terms ‘short’ and ‘long’ imply the ratio between the SL period and the wavelength of scattered light). It is shown that in the case of long-period SL there are two  $A_1(TO)$  modes: one with frequency equal to the  $A_1(TO)$  phonon in bulk GaN and another one with frequency equal to the interface phonon on the isolated AlN/GaN heterojunction. The established dependence between frequency splitting and the SL period can be well approximated by exponential function.



**Figure 3.** (a): A<sub>1</sub>(TO) Raman spectra of the GaN/Al<sub>0.28</sub>Ga<sub>0.72</sub>N SLs with  $d_1 = d_2$  and different  $d = d_1 + d_2$ . Corresponding  $s$  values are as follows:  $s = 0.25$  (2.5/2.5), 0.5 (5/5), 1 (10/10), 2 (20/20), 4 (40/40), 8 (80/80), 16 (160/160), 32 (320/320), 150 (1500/1500). Positions of the A<sub>1</sub>(TO) lines in bulk constituents are shown by dotted vertical lines. (b): calculated frequency splitting values in dependence on the  $s$ -parameter.

## References

- [1] Nikishin S, Holtz M and Temkin H 2005 *Jpn. J. Appl. Phys.*, **44**, 7221
- [2] Hofstetter D, Baumann E, Giorgetta F R, Dawlaty J, George P A, Rana F, Guillot F and Monroy E 2008 *Appl. Phys. Lett.*, **92**, 231104
- [3] Smirnov M B, Karpov S V, Davydov V Yu, Smirnov A N, Zavarin E E, and Lundin V V 2005 *Phys. Solid State* **47**, 742
- [4] Nikishin S, Holtz M, and Temkin H 2005 *Jpn. J. Appl. Phys.* **44**, 7221
- [5] Nakada N, Ishikawa H, Egawa T and Jimbo T 2003 *Jpn. J. Appl. Phys.* **42**, L144
- [6] Khan A, Balakrishnan K and Katona T 2008 *Nature Photonics* **2**, 77
- [7] Gleize J, Renucci M A, Frandon J and Demangeot F 1999 *Phys. Rev. B*, **60**, 15985
- [8] Rytov S M 1956 *Sov. Phys. JETP*, **2**, 466
- [9] Kitaev Yu E, Limonov M F, Tronc P and Yushin G N 1998 *Phys. Rev. B*, **57**, 14209
- [10] Loudon R 1964 *Adv. Phys.*, **13**, 423
- [11] Kuball M, Hayes J M, Prins A D, van Uden N W A, Dunstan D J, Shi Y and Edgar J H 2001 *Appl. Phys. Lett.*, **78**, 724
- [12] Davydov V Yu, Kitaev Yu E, Goncharuk I E, Smirnov A N, Graul J, Semchinova O, Uffmann D, Smirnov M B, Mirgorodsky A P and Evarestov R A 1998 *Phys. Rev. B*, **58**, 12899
- [13] Collins A T, Leitowlers E C and Dean P J 1967 *Phys. Rev. B*, **158**, 833
- [14] Misek J, and Srobar F 1979 *Elektrotech. Cas.*, **30**, 690
- [15] Lee B C, Kim K W, Strocio M A, and Dutta M 1998 *Phys. Rev. B*, **58**, 4860