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Abstract. The results of joint theoretical and experimental studies aimed at revealing features in the Raman spectra, which can be used for evaluation of the interface quality between GaN and AlN layers in short-period GaN/AlN superlattices (SLs) are presented. The Raman spectra for SLs with sharp interface and with different degree of interface diffusion are simulated by *ab initio* calculations and within the framework of random-element isodisplacement model, respectively. The comparison of the results of theoretical calculations and experimental data obtained on PA MBE and MOVPE grown SLs, leads to conclusion that the spectral region of the A_1(LO) confined phonons is very sensitive to the degree of interface sharpness. As a result of comprehensive studies, the correlations between the parameters of the A_1(LO) confined phonons and the structure of SLs are obtained. The results of the complex studies can be used to optimize the parameters of the growth process in order to form structurally perfect short-period GaN/AlN SLs.

1. Introduction

The operation of modern optoelectronic and electronic devices incorporating the (Al,Ga)N-based quantum-well heterostructures critically depends on the composition perfection of the constituent layers and the quality of the interfaces between them. The first problem can be solved by replacing ternary compound layers both in active and emitter regions of devices with short-period superlattices (SLs) formed by binary GaN/AlN compounds with layer thicknesses varied with an accuracy at the submonolayer level (1 monolayer (ML) = 0.25 nm) [1,2]. In this case, the stringent requirements are imposed on the quality of the interfaces between the constituent GaN and AlN layers, namely, to ensure the sharpness of the upper and lower heterointerfaces, as well as to achieve their atomic smoothness with a root-mean-square deviation of the surface roughness profile at the level of 1–2 ML over an area of several square micron. The development of new non-destructive methods for quantitative diagnostics of such structures is a very urgent task. Raman spectroscopy is a recognized tool for the non-destructive study of the phonon spectrum of superlattices (SLs). In a number of works it has been shown that this technique can be successfully used to quantify such important structural parameters of short-period GaN/AlN SLs as their period, thickness of GaN and AlN layers, sign and magnitude of strain in these layers, and other characteristics [3–5]. However, as far as we know, there are no data in the literature on the possibility of assessing the degree of interface sharpness in short-period wurtzite GaN/AlN SLs using Raman spectroscopy data.

In this work, we present the results of complex theoretical and experimental studies aimed at revealing features in the Raman spectra, which can be used for evaluation of the interface sharpness degree between GaN and AlN layers in wurtzite GaN/AlN SLs. The aim of our research is to obtain scientifically-based recommendations for optimizing the technology for growing high-quality epitaxial III-nitride heterostructures.

2. Experimental and Calculation Details

Short-period equal-thickness SLs $(GaN)_m/(AlN)_m$ (where m is the number of monolayers; m = 4,6,8) were studied both experimentally and theoretically. Two techniques were employed for the SL growth, namely plasma-assisted molecular beam epitaxy (PA MBE) using Setup Compact 21T (Riber, France) equipped with a N_2-plasma source HD-25 (Oxford Appl. Res. Ltd., UK) and metal-organic vapor phase epitaxy (MOVPE) using a system with a horizontal-flow inductively heated single-wafer reactor (strongly redesigned Epiquip VP-50RP (Epigress, Sweden)).

The Raman measurements were performed at room temperature using a T64000 (Horiba Jobin-Yvon, Lille, France) spectrometer equipped with a confocal microscope. The line at 532 nm (2.33 eV) of Nd: YAG laser (Torus, Laser Quantum, Inc., UK) was used as the excitation source. All spectra were measured in a backscattering geometry $z(xx)\bar{z}$. Here, z is the direction of the 3-fold optical axis, and x and y are mutually orthogonal axes, which are arbitrarily oriented in the substrate plane.

The *ab initio* calculations using the plane-wave pseudopotential method were carried out within the framework of density functional theory in the local density approximation (DFT-LDA) as realized in the ABINIT software package [6, 7]. The phonon wave vectors and frequencies were obtained in the Γ-point of the BZ within the density functional perturbation theory (DFPT) [8]. The Raman spectra of SLs with sharp interfaces were simulated from the Raman tensor whose components are the third-order total-energy derivatives (with respect to the electric field and the atomic displacements) calculated within perturbation theory by applying the $(2n + 1)$ theorem [9].

The diffusion of sharp interfaces in binary SLs implies the presence of regions with random occupation of cation positions. Modeling the dynamics of such systems using *ab initio* calculations is a difficult task associated with the use of large supercells. At the same time, within the framework of classical lattice dynamics based on the use of model interatomic potentials, an approach has been developed that makes it possible, without special computational costs, to simulate phonon states and vibrational spectra of crystals with random occupation of positions by different atoms, that is, solid solutions. The idea behind a method called random-element isodisplacement (REI) dates back to [10]. In particular, this approach has been successfully applied in modeling the phonon spectra of solid solutions of AlGaN [11]. In the present work, we applied a similar approach to model the phonon states in binary GaN/AlN SLs with diffuse interfaces.

3. Results and Discussion

3.1. Growth

The SLs with the total thickness of about 500 nm were grown on *c*-sapphire substrates. The quality of interfaces in GaN/AlN heterostructures is determined by the applied epitaxial technology with different surface mobility of precursors (adatoms) and the rate of switching the growth fluxes. In addition, sharpness of heterointerfaces strongly depends on atomic segregation due to different binding energy between Ga and Al atoms with nitrogen [12-14]. Finally, elastic strain (-2.5%) in GaN/AlN heterostructure can induce the transition from two dimensional to three dimensional (2D-3D) growth. All processes at the GaN/AlN interface strongly depend on the growth conditions, and the substrate temperature plays a decisive role either in the acceleration of the processes or, conversely, in their kinetic limitation.

When using PA MBE, the growth of AlN buffer layers starts on annealed and nitrided substrates. Then, using epitaxy with increased mobility at a substrate temperature of 780°C, a nucleus layer with

the thickness of 65 nm was formed on these substrates, and afterwards, using metal-modulated epitaxy at the same temperature, the buffer layers with thicknesses of about 300 nm were grown as described in [15]. The SLs were grown at relatively low growth temperatures of 690–700°C at metal-enriched conditions with the FIII/FN_2* flux ratio above 1 followed by periodic annealing of the excess metallic (Ga) phase in accordance with the approach described in [16].

The low growth temperature of PA MBE (690-700°C) used in this work ensured kinetic suppression of the Ga segregation effect, which usually blurs the upper interface of GaN/AlN quantum wells at higher temperatures (>720°C). Moreover, the low growth temperature limits the possible transition from 2D to 3D growth mode. To maintain the 2D-growth mechanism at the low temperatures, we used the metal-enriched PA MBE growth conditions, which increase the surface mobilities of both Group III and nitrogen atoms due to the formation of a double Group III adlayer on the III-N surface [16]. In addition, the high switching rate of Ga and Al fluxes (<0.3 s) incident on the substrate provided the sharpness of the interfaces in the samples grown using PA MBE at ultra-low N_2-pressure $<2\times10^{-5}$ Torr.

MOVPE structures were grown using trimethylgallium (TMGa), trimethylaluminum (TMAl) and ammonia (NH_3) as precursors. Reactor pressure was kept at 100 mbar through the whole process. Epitaxial process was started by growth of 130nm thick AlN buffer layer on (0001) sapphire substrates at 980ºC with 0.11nm/sec growth rate. AlN/GaN SLs were grown at 1030°C (typical growth temperature for GaN in our reactor). The growth duration of the GaN layers was varied in the range of 3–6 seconds while for AlN it was 10–24 sec. A decrease of the SL period was reached by a reduction of the growth time of individual layers and the shortest period has been achieved also by a reduction of TMGa and TMAl flows. Very low NH_3 flows are preferable for the AlN growth, while for the GaN growth, the NH_3 flow should be about 1/3 of a total gas flow though the reactor. In our case, the NH_3 flow was 3.5 SLM for the GaN growth and 20 sccm (standard cubic centimeter per minute) for AlN. Usually H_2 is used as a carrier gas for the GaN growth. However, it is well known that GaN is etched by hydrogen in H_2/NH_3 mixtures and etching rate is rapidly increased with the reduction of NH_3 concentration [17]. Under very low ammonia flow used for the AlN growth, the GaN etching rate at the very beginning of the AlN growth is much larger that the AlN growth rate. It inevitably leads to the destruction of the GaN surface and the formation of intermediate AlGaN layers. For suppression of this undesirable process different carrier gases were used for growth of GaN and AlN layers of SL structures. For GaN it was a mixture of 5.5 SLM (standard liter per minute) of N_2 and 1 SLM of H_2 while for AlN it was N_2 with a flow of 8.2 SLM.

3.2 Raman measurements, ab initio and REI calculations

As will be shown below, the differences in the Raman spectra of SLs grown by PA MBE and MOVPE are most clearly manifested in the spectral region in which LO phonons make the largest contribution. The theory based on the assumption of an ideally sharp interface, that is, on a model in which there is no interlayer diffusion of cations, predicts for such phonons the character of standing waves strictly localized in layers of the corresponding materials. As a result, the Raman spectra of SLs in the frequency range of such phonons contain two sets of lines in frequency ranges phonon modes from B_1 to A_1(LO) of bulk materials. By the number of such lines, one can estimate the thickness of the corresponding layers [18].The Raman spectra bands corresponding to these vibrational modes should be observed in the $z(xx)\bar{z}$ scattering geometry. Since the frequency ranges of modes with A_1(LO) symmetry slightly overlap for bulk GaN and AlN crystals, the GaN-like modes should appear in the 690–733 cm^{-1} range, whereas the AlN-like modes in the 719–875 cm^{-1} range.

Figure 1 shows the results of *ab initio* calculations of Raman spectra of the $(GaN)_m/(AlN)_m$ (m = 4,6,8) SLs in the spectral region of A_1(LO) modes. The calculations were performed under the assumption of sharp interfaces between the SL layers, with a detailed description of such calculations given in [16]. The same figure shows the experimental Raman spectra for the $(GaN)_m/(AlN)_m$ (m = 4,6,8) SLs grown by PA MBE and MOVPE methods. As can be seen, a good agreement is observed

between the *ab initio* simulated spectra and the experimental spectra measured on the SLs grown by PA MBE, which indicates the presence of sharp interfaces in the latter.

However, the experimental spectra for the SLs grown by MOVPE differ significantly from the spectra calculated *ab initio*. The difference becomes more and more noticeable as the total SL period, that is, the layer thickness, decreases. With a decrease in the SL period, the following changes are observed: the frequency interval in which Raman active modes of A_1(LO) symmetry appear decreases; the number of distinguishable spectral peaks decreases; their intensities become approximately the same; the intensity of the ~ 750 cm^{-1} line, which is traditionally interpreted as the longest standing wave in the GaN layer, drops sharply. This behavior prompted us to assume that there is a significant interlayer diffusion of cations in SLs grown by the MOVPE method, and their interfaces differ from the sharp ones.

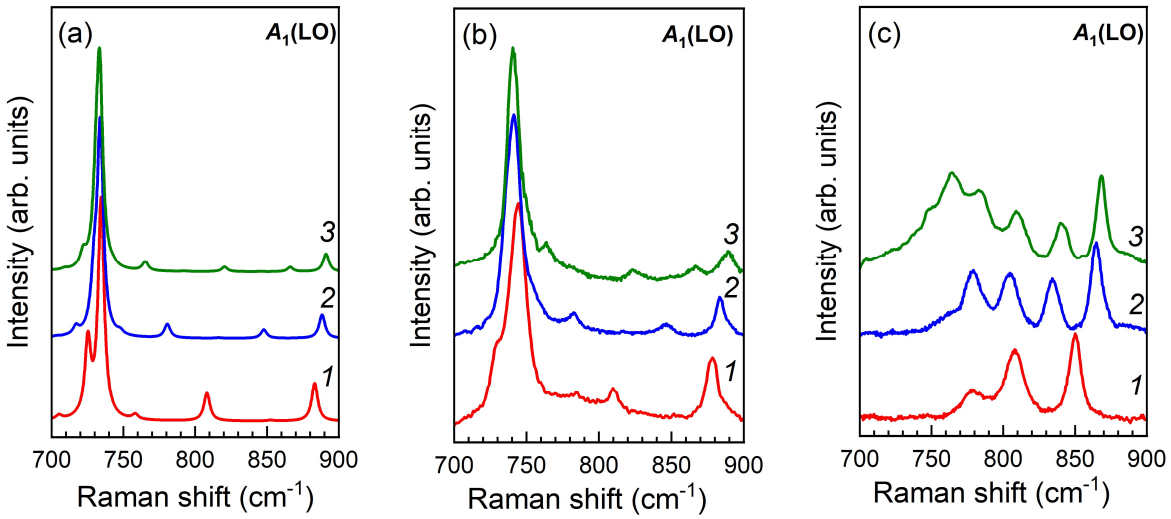

Figure 1. Calculated (*a*), and experimental (*b*, *c*) Raman spectra of $(GaN)_m/(AlN)_m$ SLs in $z(xx)\bar{z}$ scattering geometry in the region of A_1(LO) modes: *1* – *m*=4, *2* – *m*=6 and *3* – *m*=8. The (GaN)/(AlN) SLs were grown by PA MBE (*b*) and MOCVD (*c*).

To test this hypothesis, we simulated the Raman spectra of SLs with diffuse interfaces. The diffuse interfaces were modeled by a $Ga_xAl_{1-x}N$ solid solution, in which the compositional parameter x is a linear function of the z - coordinate along the growth axis of the planar heterostructure. Keeping the SL period, we varied the modulation profile simulating SL with various degrees of interface diffusion.

The idea of the REI method, which we applied to the modeling of phonon states in GaN/AlN SLs with diffuse interfaces, is to use the concept of a "split" atom. If a given Wyckoff position can be occupied by an atom *A* with a probability *a* or an atom *B* with a probability *b*, then in writing the equations of motion of atoms we can assume that this position contains *two* non-interacting atoms with masses *aA* and *bB*. In the equations of motion, the force constants calculated for atoms *A* and *B* are also multiplied by factors *a* and *b*, respectively. Due to the use of the split atom concept, the number of equations and the number of solutions obtained increases. Some of the solutions correspond to the vibrations in which atoms *A* and *B* move in phase. They describe real vibrations of a structurally disordered system. Other solutions correspond to the vibrations in which atoms *A* and *B* move in antiphase. They describe localized vibrations induced by structural disorder. Such modes are of particular interest when one type of atoms corresponds to a low-concentration impurity.

In this work, we used atom–atom potentials that were previously successfully used in modeling the lattice dynamics of both bulk GaN and AlN crystals and binary SLs with sharp interfaces [18]. These potentials are based on the hard-ion approximation and include both the Coulomb long-range action

and the non-Coulomb short-range action described in the framework of the Born-Karman model. The parameters of the Born-Karman model $A = \frac{d^2E}{dR^2}$ and $B = \frac{1}{R}\frac{dE}{dR}$, borrowed from potential models of bulk crystals of GaN and AlN, are given in Table 1. Here E is the energy and R is the bond length, given in newton per meter (N/m).

Table 1. Parameters of the Born-Karman potentials (in N/m).

Interacting atoms	A	B
Ga-N	230	-15
Al-N	240	-8
N-N	10	0
Ga-Ga	15	0
Al-Al	15	0

The cation effective charges determined from the LO-TO splitting are Z(Ga) = 1.14e and Z(Al) = 1.27e. The charges on nitrogen atoms were taken depending on their positions with respect to the cations. The effective charge of the N atom located in the center of the $N\text{Ga}_{n1}\text{Al}_{n2}$ tetrahedron was taken equal to $Z(\text{N}) = -\frac{1}{4}\left(n_1 Z(\text{Ga}) + n_2 Z(\text{Al})\right)$

The SL structural parameters were assumed to be independent of its total period. Thus, the size of the hexagonal unit cell in the interface plane was taken to be 3.15 Å, and the distance along the hexagonal axis between the cation adjacent layers was taken to be 2.5 Å. Raman line intensities were calculated using the polarizable bond model. The details of such calculation are described in [18].

Using the model described above, we calculated the phonon spectra of the $(\text{GaN})_m/(\text{AlN})_m$ (m = 4,6,8) SLs with different degrees of interface diffusion. Note that, within the framework of the REI model used by us, at any degree of the interface diffusion, the axial symmetry (C_{3v}) of the structure is not violated. The BZ-center phonons in such structures can be divided into A-phonons, in which atoms move along the main axis, and E-phonons polarized in the interface plane. When modeling Raman spectra, special attention was paid to the scattering geometry $z(xx)\bar{z}$. In this geometry, the E(TO) and A(LO) phonons are active in Raman scattering.

Figure 2 shows the results obtained. Here, parameter I is the interface thickness (the number of monolayers in which Ga and Al atoms are simultaneously present). Note that the spectra calculated in the REI model under the assumption of a sharp interface (I = 0) are in very good agreement with the *ab initio* calculated spectra under the assumption of a sharp interface. This gives reason to believe that the REI model should adequately reflect the features of SLs with diffused interfaces. An analysis of atomic displacement patterns revealed that as the degree of interface diffusion increases, the modes localized in the GaN and AlN layers begin to mix. This leads to a significant change in the Raman spectrum. The intensities of the main lines corresponding to the A_1(LO)-GaN and A_1(LO)-AlN modes decrease, while the scattering intensities at other harmonics increase. Along with this, the frequency interval occupied by these peaks is gradually narrowing. Additional calculations show, that with further diffusion of the interfaces, the structure becomes similar to a solid solution with a profiled concentration. In this case, the number of lines in the Raman spectrum in the region of A_1(LO) phonons decreases. Ultimately, the SL spectrum becomes similar to the spectrum of a homogeneous solid solution with a concentration of 50/50, in which one single A_1(LO)) line with a frequency of ~ 820 cm^{-1} is present [13].

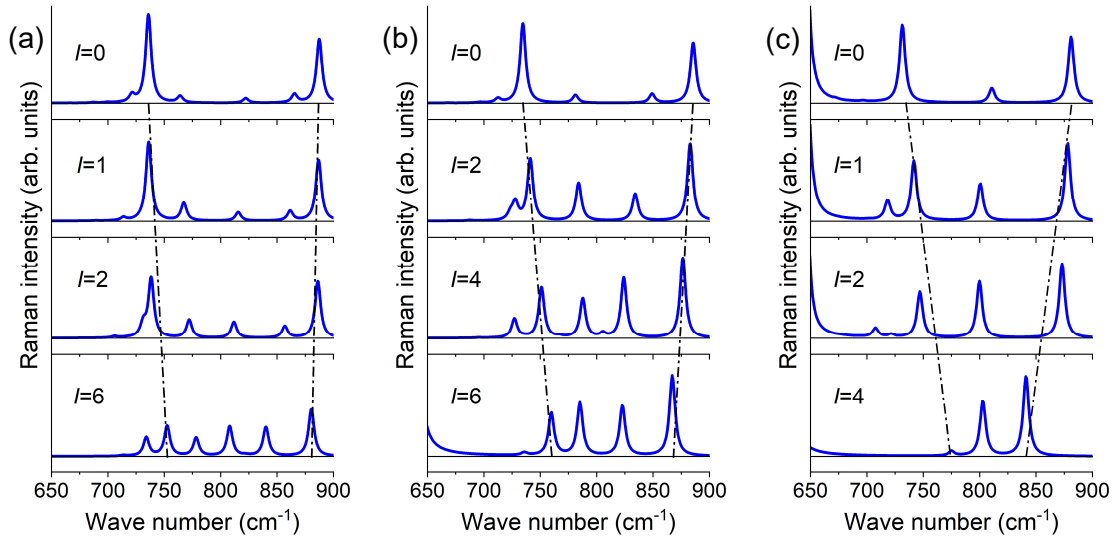

Figure 2. Calculated Raman spectra of $(GaN)_m/(AlN)_m$ SLs in the $z(xx)\bar{z}$ scattering geometry in the region of A_1(LO) modes: (*a*) – *m*=8, (*b*) – *m*=6, (*c*) – *m*=4.

Qualitatively, the results of calculations within the framework of the REI model reflect all the main trends in the spectra of samples grown by the MOVPE method. To verify this, let us compare the experimental spectra with the results of calculations for *I*= 4, 6, and 6 for *m*= 4, 6, and 8, respectively, as is done in figure 3. It can be seen, that both in the calculation and in the experiment, the same changes are observed: as the SL period decreases, the number of lines decreases, the highest-frequency line shifts to the lower frequencies, and the lowest-frequency line shifts to the higher frequencies. In addition, the calculation correctly reproduces a sharp decrease in the intensity of the line at ~750 cm^{-1}. These results confirm the validity of the assumption made about the interface diffusion in MOVPE grown SLs and make it possible, by choosing the interface diffusion parameter that best reproduces the observed spectrum, to estimate the interface thickness in each of the studied SLs.

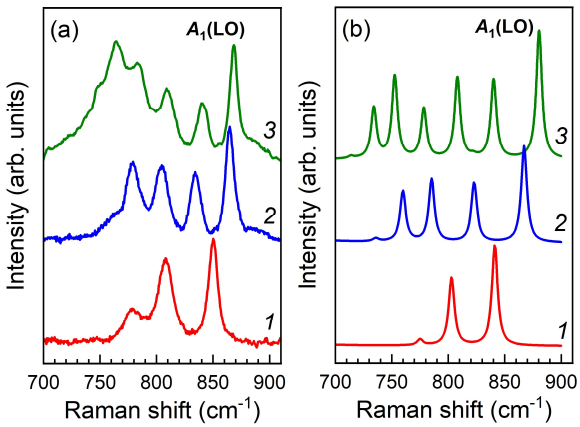

Figure 3. Experimental $z(xx)\bar{z}$ Raman spectra of $(GaN)_m/(AlN)_m$ SLs grown MOVPE: *1* – *m*=4; *2* – *m*=6; *3* – *m*=8 (*a*) in comparison with the spectra calculated for the same SLs within the REI model with *I*=4, 6, and 6 for *m*=4, 6, and 8, respectively (*b*).

4. Conclusion

Summarizing, a combination of theoretical analysis and experimental Raman studies allowed us to reveal features in the Raman spectra, which have been used for characterization of the interface quality between GaN and AlN layers in wurtzite short-period GaN/AlN SLs. Raman experiments were performed on short-period SLs grown by PA MBE and MOVPE. A good agreement was obtained between the spectra simulated *ab initio* under the assumption of sharp interfaces and the experimental

spectra measured on the SLs grown by PA MBE. However, the experimental spectra of the SLs grown by MOVPE differ significantly from the spectra simulated *ab initio.* To test the hypothesis of significant interlayer diffusion of cations in the SLs grown by MOVPE, we simulated the Raman spectra of SLs with a random occupation of atomic positions within the interface using REI method. Keeping the SL period, we varied the modulation profile, simulating SLs with different degrees of interface diffusion. It was found that the results of calculations within the framework of the REI model reflect all the main trends in the spectra of samples grown by MOVPE. These results confirm the model of the interface diffusion in SLs grown using MOVPE, and made it possible to estimate the interface thickness by choosing the interface diffusion parameter that best reproduces the observed SL spectrum. The results of these studies open up new possibilities for evaluating the structural parameters of short-period GaN/AlN SLs using Raman spectroscopy and can be used to optimize the growth parameters of structurally perfect III-nitride heterostructures.

Acknowledgments
This research was supported within the State Assignments from the Ministry of Science and Higher Education of the Russian Federation to the Ioffe Institute (0040-2019-0006).

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