Raman spectra of interface phonons in long-period AlN/GaN superlattices as a tool for determination of the structure period

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Abstract. AlN/GaN superlattices (SL) grown by metalorganic vapor-phase epitaxy with the period of SLs varied from 20 nm to 140 nm, and the thickness of the structures ranged from 0.7 to 1 µm were studied by polarized Raman spectroscopy technique. The peaks within a complex spectral feature of the symmetry A\textsubscript{1}(TO) observed at about 580 cm\textsuperscript{-1}, were assigned to the interface and quasi-confined phonons. Frequency splitting between the peaks was found monotonously increasing along with the SL period. This dependence was explained using the dielectric continuum model. A method based on this finding was proposed for estimating the period SL using Raman spectroscopy. This method extends the traditional approach based on the studies of folded acoustic phonons in the short-period SLs.

1. Introduction

A\textsubscript{III}B\textsubscript{V} nitrides attract much attention owing to their unique physical properties of great potentiality for modern optoelectronics. AlN/GaN superlattices are widely used as an active material in various devices operating in ultraviolet and infrared spectral regions. They are used in deep-ultraviolet light emitting diodes and as photodetectors [1, 2]. Fine tuning of the devices requires the SLs with strictly controlled structural parameters. Raman spectroscopy is an efficient technique for the fast and 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 polar modes strongly depend on the layer thickness [3, 4]. This phenomenon opens up the possibility to use Raman spectroscopy for characterization of such structures. Thereby it is important to establish precise quantitative relations between phonon frequencies and structural parameters. Much attention was paid to the short-period SLs which are rather promising for the application purposes. The ratio of the layer thicknesses was considered as the most important structural parameter which can be reliably determined from the polarized Raman spectra [4]. However the most pressing issue is determination of the absolute values of the layer thicknesses and period. For this purpose one customary uses the folded acoustic branches [5]. This method is quite efficient for the SLs with a period below 10 nm. For longer periods, the frequencies of the folded acoustic phonons become too low to be reliably determined [6]. This obstacle stimulates searching of another approach. This paper is aimed at developing and testing the new approach suitable for the long-period SLs.
2. Experimental details

AlN/GaN SLs were grown by metalorganic vapor phase epitaxy in a horizontal flow reactor at temperature of 1050 °C on Al₂O₃ using a double AlN-GaN buffer layer [7]. The studied samples had the equal thickness of the GaN and AlN layers, the SL period (d) varied from 20 nm to 140 nm, and the total thickness of the structures ranged from 0.7 to 1 µm. In total, the set comprised 6 samples. According to the d value, we shall refer the samples as S20, S40, S60, S80, S100 and S140.

The group-symmetry analysis of the recorded polarized Raman spectra allowed assigning all observed spectral features to the transversal (TO) or longitudinal (LO) phonon modes of different irreducible representations. As it was previously shown, all optical modes in the short-period binary SLs can be divided into two groups: the confined modes (C) localized within the layers of particular composition and the interface modes (IF) localized in the vicinity of interfaces. Spectroscopic manifestations of the C-modes were discussed in Ref. [5]. This paper reports the results concerning the IF-modes.

3. Theoretical background

Quantitative description for the polar phonons in planar heterostructures is usually based on the Dielectric Continuum Model (DCM) [8]. In the framework of this model, the discrete crystal structures of the layers are replaced by continuous media with dielectric functions, which represent the phonon contributions of the corresponding crystals:

\[ \varepsilon(\omega) = \varepsilon^{\infty} \frac{\omega_{\text{LO}}^2 - \omega^2}{\omega_{\text{TO}}^2 - \omega^2} \]  

The parameters \( \varepsilon^{\infty} \), \( \omega_{\text{TO}} \) and \( \omega_{\text{LO}} \) are borrowed from phonon spectra of the bulk GaN and AlN crystals. By solving the Maxwell equations, the spectrum of the polar phonons in a layered AlN/GaN heterostructure can be determined [3]. The resulting solutions allow studying the influence of the SL structure on phonon spectrum.

![Figure 1. Dependencies of phonon frequencies of the IF and QC modes on the layer thickness ratio in a short-period SL (a) and in a medium-period SL (b). The anti-crossing points are shown in panel (a) by circles. The IF-QC frequency splitting is shown in panel (b) by arrows.](image-url)
The structure-spectrum dependence is relatively simple for a short-period SL in which the SL period is much shorter than the phonon wavelength. In such case [4], the phonon modes propagating along the SL axis are C-modes, and their frequencies are almost independent on the SL structure. Contrariwise, the phonon modes propagating in the interface plane are IF-modes. Frequencies of these modes strongly depend on the layer thickness ratio monotonously varying between TO-AlN and TO-GaN (or between LO-AlN and LO-GaN) values. The situation is a little bit more complex for the SL built of the anisotropic media such as the wurtzite-like GaN and AlN crystals. In such case the TO and LO frequencies for the C-modes and IF-modes are different, and a new type of modes appears. These are the so called quasi-confined (QC) modes which have confined character in one layer and propagating character in another. The frequency intervals for the IF and QC modes are shown in figure 1a. The calculated frequencies of the IF and QC modes are shown in the figure 1 in dependence on the structural parameter \( f = \frac{d_{\text{AlN}}}{(d_{\text{AlN}} + d_{\text{GaN}})} \), where \( d_{\text{AlN}} \) and \( d_{\text{GaN}} \) are the thicknesses of AlN and GaN layers correspondingly. This parameter characterizes the layer thickness ratio. The total SL period is characterized by the parameter \( s = kd \), in which \( k \) is the phonon wave vector. Figures 1a and 1b correspond to the short-period SLs (\( s = 0.1 \)) and the medium-period SL (\( s = 2 \)).

One can see that the QC and IF modes smoothly transform one to another in the former case (see figure 1a) whereas they exhibit the anti-crossing behavior in the latter case (see figure 1b). Magnitude of the frequency splitting depends on the SL period. The dependence can be used to estimate the SL period from the Raman spectroscopy data.

4. Results and discussion

Figure 1 shows that there are two anti-crossing points: one within the TO-frequency interval and another one within the LO-frequency interval. The former is close to the \( f = 0.5 \) value, i.e. the SL with \( d_{\text{AlN}} = d_{\text{GaN}} = d \). Such equi-period SLs are mostly widespread among the real synthesized samples, and the IF-modes within the TO-frequency interval are well resolved. Besides, these modes are weakly dependent on the elastic strain [9]. Taking into account all these facts, below we focus our attention on the IF-QC splitting in the vicinity of the \( E_1(\text{TO}) \)-GaN frequency.

![Figure 2](image-url)

**Figure 2.** Raman spectra of the S20 (a) and S140 (b) samples recorded in \( \chi(zz)\overline{x} \) geometry. The insets show the decomposition of the spectrum into several Lorentz-type components. The IF-QC frequency splitting \( \Delta \omega \) is indicated by horizontal arrow.

The IF modes in the TO-frequency interval can be found in the Raman spectra recorded within \( \chi(zz)\overline{x} \) geometry. Experimentally studied Raman spectra of all considered samples contain complex spectral features in the 560–600 cm\(^{-1}\) range. Two of the spectra are shown in figure 2. It is seen that the band between 560–600 cm\(^{-1}\) has a multi-mode character. Spectral analysis based on decomposition of the band into the Lorentz-type components allowed us to identify the peaks corresponding to the IF and QC modes, as it is shown in the insets. On selecting the spectral components corresponding to the
QC an IF modes we neglect the components which leak from other symmetry species (they are shown by dashed lines).

The error in determining the frequency of $\omega_{\text{IF}}$ and $\omega_{\text{QC}}$ depends both on the accuracy of registration the experimental spectra and on the quality of the fitting procedure. Accuracy of the registration of the Raman spectrum is within 1–2 cm$^{-1}$. The correctness of the fitting procedure is usually characterized by a mismatch (DIS). In infrared and Raman spectroscopy, the fit is usually considered good if the DIS value does not exceed 2% [10]. In our cases, the DIS values obtained by fitting the spectra depend on the complexity of the analyzed spectral feature and vary in the range of 0.5–1.5 %. It is reasonable to assume that it is DIS, which characterizes the error of determination of the fitting parameters. Thus, the estimated errors of the determined $\omega_{\text{IF}} - \omega_{\text{QC}}$ splitting values, which comprise both measurement inaccuracies and inaccuracies of the fitting procedure, were found within 3–9 cm$^{-1}$. They are shown in figure 3.

![Figure 3. IF-QC frequency splitting $\Delta\omega$ in dependence on the SL period: experimental data (symbols) and theoretical estimation (solid line). Estimated errors (comprising both the measurements and the fitting procedure inaccuracies) are shown by vertical bars.](image)

The measured frequency splitting between IF and QC components is represented in figure 3 in dependence on the SL period $d$ ranging from 20 to 140 nm. Raman measurements were done in the backscattering geometry with excitation $\lambda=532$ nm. Therefore, the dimensionless parameter $s = kd$ takes the values in the range 1–8. In accordance with the figure 1, such variation of $s$ parameter should significantly change the IF-QC splitting. The calculated values are shown in figure 3 by solid line. Theoretical dependency demonstrates a monotonically increasing character with a saturation behavior in the long-period limit. The limit value $\Delta\omega$ corresponds to the difference $\omega(\text{IF}) - \omega(\text{A}_1(\text{TO})-\text{GaN})$ in which $\omega(\text{IF})=578$ cm$^{-1}$ is the frequency of the IF mode in an isolated AlN/GaN heterojunction. It is hardly possible to distinguish the same saturation tendency in the experimental data due to the limited set of the samples. However, it can be seen that the experimental data correlate with the theoretical prediction derived from the DCM simulation.

In order to understand the nature of the IF-QC splitting let us consider spatial pattern of the involved phonon modes. Within the framework of DCM method, the electric field strength (EFS) and the phonon amplitude depend on the $z$ coordinate (which is directed along the SL axis. The EFS($z$) dependencies calculated for the S20 and S140 SLs are shown in figure 4.

It can be seen that the EFS induced by the IF and QC modes are close to each other in the medium-period SL (figures 4a and 4c) and differ markedly in the long-period SL (figures 4b and 4d). It can also be seen that the electric field induced by both modes in the AlN layer is not sensitive to the SL period. This is due to the fact that vibrational frequency is out of range of the characteristic AlN polar modes. On the contrary, the vibrational amplitudes within GaN layer are very sensitive to the frequency in the vicinity of the E$_1$(TO)-GaN value. Recall that the dielectric function has a singularity at this frequency. Figure 4d evidences that the strength of the longitudinal electric field induced by QC mode greatly increases with SL period. This fact explains why the QC component dominates in the Raman spectra of the long-period SL as it takes place in figure 2.
5. Conclusion

The results presented in this study demonstrate that the polarized Raman spectra of the long-period AlN/GaN SLs provide valuable information for estimating not only the layer thickness ratio but also the total SL period. The latter opportunity is related to the frequency splitting effect which involves the interface and quasi-confined phonon modes. The split Raman lines can be resolved experimentally and the magnitude of the splitting can be reliably related with the SL period. The relation was derived from the Dielectric Continuum Model and was confirmed by comparison with experimental data. The proposed method deals with polar optic modes in the medium frequency interval of the Raman spectra. It is rather efficient for the SLs with a period larger than 10 nm and thus can be considered as an effective extension of the traditional approach based on the folded acoustic phonon study in short-period SLs.

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