Infrared generalized ellipsometry on non-polar and superlattice group-III nitride films: strain and phonon anisotropy

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This contribution reviews the application of generalized infrared spectroscopic ellipsometry (GIRSE) to studies of optical phonons in heteroepitaxial wurtzite GaN films with a-plane orientation and c-plane Al(Ga)N/GaN superlattices. We demonstrate the capability of GIRSE to detect spectrally narrow dichroism, caused by anisotropic strain in non-polar oriented films thereby allowing a precise location of the phonon mode resonances for different polarizations. A distinct correlation between anisotropic strain components, which have been independently assessed by high-resolution X-ray diffraction, and phonon frequencies reveal the phonon deformation potentials. Further, GIRSE is shown to be a valuable tool in identification of superlattice phonon modes and their character. The frequency shifts of the superlattice modes with respect to the strain-free positions are analyzed versus strain and composition in order to assess the mode suitability for estimation of strain, polarization doping, and composition for the individual layers in complex device heterostructures.
1 Introduction

The advent of group-III nitride semiconductors AlN, GaN, InN and their alloys has undoubtedly started a new era in semiconductor technology with a large impact on science and everyday life [1]. Due to their direct band gaps (0.67 eV for InN, 3.4 eV for GaN and 6.0 eV for AlN), and the possibility of alloying, group-III nitrides have become materials of key importance for optoelectronic applications in the visible and ultraviolet region, as well as for high-power and high-temperature electronics. Despite remarkable progress, group-III nitride technology faces several critical issues that hinder further developments. The most severe is the lack of native substrates and consequently the need to grow the materials on mismatched substrates, which results in the presence of strain in films and low-dimensional structures.

Strain in semiconducting materials has a significant impact on their fundamental properties and characteristics as it may change the crystal symmetry, and also the electronic band-structure and phonon spectrum for example. Strain in semiconductor superlattices (SLs) affects their complex lattice dynamics and further complicates the interpretation of their vibrational spectra. The latter holds explicitly for piezoelectric SLs, e.g., based on group-III nitrides, where unambiguous identification and assignment of phonon modes is hindered by the competing effects of strain, composition, and strain-induced polarization fields on phonon frequencies.

Phonon modes in strained films shift or split with respect to the modes of unstrained material according to intrinsic deformation potentials, which provide distinct fingerprints for evaluation of the complex strain state. In addition, phonon parameters can be used to obtain information on alloy composition, free-carrier concentration, and mobility in individual layers of device heterostructures [2]. This paper demonstrates the viability of generalized infrared spectroscopic ellipsometry (GIRSE) to assess strain components, composition, and polarization field effects in wurtzite-structure III-nitride films with non-polar surface orientations and low-dimensional structures. Two exemplary cases of particular technological importance are chosen: a-plane GaN films and c-plane Al(Ga)N/GaN SLs.

1.1 a-plane GaN films

The presence of large piezoelectric and spontaneous polarizations in wurtzite-structure...
group-III nitride materials generates electric fields across heterostructures grown along the polar optical axis [3]. Consequently, an uncontrolled shift of the emission peaks and a reduction of the emission efficiency occur in photonic devices such as light emitting diodes (LEDs). Strategies to overcome these problems by growing bulk materials and device heterostructures with non-polar surface orientations are currently under intense investigation [4]. In such instances, however, non-polar nitride films experience anisotropic biaxial strain as a consequence of the anisotropy of the growth surfaces [5]. Assessment of anisotropic strain components using phonon frequencies in non-polar III-nitride films requires detailed knowledge of material vibrational properties, anisotropic strain effects, and phonon deformation potentials. Most of these, however, remain unknown or highly controversial [5–8]. GIRSE is an excellent tool for anisotropic materials characterization allowing access to the complete set of polar phonons in non-c-axis oriented group-III nitrides [9].

1.2 Al(Ga)N/GaN superlattices AlGaN/GaN SLs  

AlGaN/GaN SLs have recently attracted much attention due to their application as active and cladding materials in state-of-the-art LEDs and laser diodes, as well as in high-frequency transistor devices. Al(Ga)N/GaN SLs are also very attractive for strain management, dislocation reduction, p-contacts, and infrared intersubband detectors. Detailed knowledge of the fundamental properties of these heterostructures is mandatory for appropriate design of devices and could be used for the characterization of complex multilayered structures. Despite the strong research interest, there are only a few reports on the vibrational properties of Al(Ga)N/GaN SLs and the phonon mode behavior of these heterostructures is still not well understood. Recent theoretical studies within the framework of the Rigid Ion Model predict the presence of localized and delocalized phonon modes in hexagonal AlN/GaN SLs [10]. The main challenge is the identification of the nature of SL phonon modes; Only few experimental studies exist and the theoretical models do not provide a consistent picture. The great advantage of GIRSE is that the mode nature may be suggested upon data analysis [11, 12]. A localized mode is such, for which the polarizability needs to be consider in one of the two SL constituents only. In contrast, a delocalized mode needs to be included in the dielectric function model for both SL constituents simultaneously.

2 Theory

2.1 Phonons in wurtzite-structure group-III nitrides

The crystalline structure of wurtzite-type group-III nitrides is described by the space group $C_{6h}$, and according to the factor group analysis the optical phonon modes in the center of the Brillouin zone belong to the irreducible representation [13]:

$$\Gamma_{opt} = \Gamma_1 + 2\Gamma_4 + 2\Gamma_6 + \Gamma_4 = A_1 + 2B_1 + E_1 + 2E_2.$$ 

The $A_1$ and $E_1$ modes are both IR and Raman active, the two-fold $E_1 (E_{1\text{low}}^\text{IR} \text{and } E_{1\text{sh}}^\text{IR})$ are only Raman active and the $B_1$ modes ($B_{1\text{low}}^\text{IR}$ and $B_{1\text{sh}}^\text{IR}$) are silent. Due to the macroscopic electric field associated with the relative atomic displacement of the longitudinal phonons, the polar $A_1$ and $E_1$ modes are split into LO and TO components.

Under strain the frequencies of the zone-center optical phonons in group-III nitrides shift and/or split with respect to the strain-free values. In the linear strain approximation the mode frequency changes are related to the strain tensor via [8, 14]:

$$\omega_{\alpha} = a_{\alpha}(e_{xx} + e_{yy}) + b_{\alpha}e_{zz},$$

$$\omega_{\alpha} = a_{\alpha}(e_{xx} + e_{yy}) + b_{\alpha}e_{zz} + c_{\alpha}[(e_{xx} - e_{yy})^2 + 4e_{zz}^2]^{1/2},$$

where $x$, $y$, and $z$ are chosen along the principle crystal axes $[11\bar{2}0]$, $[\bar{1}T00]$, and $[0001]$, respectively. The silent $B_1$ mode obeys a similar relation with strain as the $A_1$ mode. The coefficients $a$, $b$, and $c$ are the corresponding mode deformation potentials per unit strain.

2.2 Generalized infrared spectroscopic ellipsometry

For a general situation of optical anisotropy, e.g., for wurtzite-structure group-III nitrides, and arbitrary sample orientation the generalized ellipsometry approach (GE) is needed. The GE parameters are described by three ratios of the polarized-light reflection coefficients among the four available complex-valued elements of the Jones reflection matrix $r$ [9]. The ratios defining the GE parameters $\Psi_{\alpha\beta}$, $\Delta_{\alpha}$ are [9]:

$$\frac{r_{\alpha\beta}}{r_{\alpha\alpha}} = \tan \Psi_{\alpha\beta} \exp(i\Delta_{\alpha}),$$

$$\frac{r_{\alpha\alpha}}{r_{\alpha\beta}} = \tan \Psi_{\alpha\alpha} \exp(i\Delta_{\alpha}),$$

and depend on the layer sequence, layer dielectric function (DF), the relative orientation of the optical axis of the anisotropic material, and the layer thickness of each single constituent in a multi-layer structure. Model calculations, which account for the layered structure of the sample, are used to obtain information on the DF spectra, thickness, and relative optical axis orientation.

2.3 Infrared dielectric model

In the infrared spectral region the DF $\varepsilon(\omega)$ is sensitive to phonon and plasmon effects. The infrared model DF can be written as a sum of lattice, $\varepsilon_{ij}^L(\omega)$ and free-charge carrier, $\varepsilon_{ij}^{FC}(\omega)$ contributions:

$$\varepsilon_{ij}(\omega) = \varepsilon_{ij}^L + \varepsilon_{ij}^{FC},$$

where $\varepsilon_{ij}^L(\omega)$ is the contribution of the phonon modes, and $\varepsilon_{ij}^{FC}(\omega)$ the contribution from free-charge carriers.
where the subscript \( j \) refers to the polarizability along the crystal principal axis.

A product-representation for harmonic oscillator line-shapes with Lorentzian broadening is employed for the calculation of the lattice contribution \( \varepsilon_j \) to the DF of uniaxial crystals, such as wurtzite-structure group-III nitrides [2, 15]:

\[
\varepsilon_j^l(\omega) = \varepsilon_{\omega,\omega} + i \gamma | \omega - \omega_j^0 |. 
\]

The anisotropic DF representations are parameterized along the principal lattice directions [5]: \( j = \begin{pmatrix} x \end{pmatrix} = \begin{pmatrix} 1120 \end{pmatrix}, j = \begin{pmatrix} y \end{pmatrix} = \begin{pmatrix} 1100 \end{pmatrix}, \) and \( j = \begin{pmatrix} z \end{pmatrix} = \begin{pmatrix} 0001 \end{pmatrix}, \) where \( \gamma_{\omega,\omega} \) denote the frequencies of the \( \varepsilon_j \) modes may be different due to different strains along \( \begin{pmatrix} x \end{pmatrix} \) - and \( \begin{pmatrix} y \end{pmatrix} \) -directions, for instance caused by anisotropic basal plane distortion. A possible contribution from free-carriers to the dielectric functions is also accounted for by the classical Drude model [16]:

\[
\varepsilon^{(fc)}_j(\omega) = -\frac{(\omega_{p,j}^0)^2}{\omega(\omega + i\gamma_{p,j})}, 
\]

with

\[
\omega_{p,j}^0 = \frac{e^2}{\varepsilon_0 m_j} \frac{N}{\varepsilon_0}, 
\]

The unscreened plasma frequency \( \omega_{p,j}^0 \) depends on the free-charge-carrier concentration \( N \) and the effective conduction band mass \( m_j \) (\( \varepsilon_0 \) is the vacuum permittivity, and \( e \) is the electrical unit charge). The plasmon broadening parameter \( \gamma_{p,j} \) is related to the optical free-carrier mobility \( \mu \):

\[
\gamma_{p,j} = \frac{e}{m_j \mu_j}. 
\]

### 3 Experimental

Various \( a \)-plane GaN films with thickness between 1 µm and 67 µm were grown on \( r \)-plane sapphire by metalorganic vapor phase epitaxy (MOVPE) and halide vapor phase epitaxy (HVPE). Crack-free 10-period AlN/GaN SLs were grown on undoped 2 µm thick GaN layers deposited on (0001) sapphire substrates by MOVPE. The structures were grown with different well thicknesses keeping the same well-to-barrier thickness ratio of 3:1. A series of 200-period Al,Ga,A,N/GaN SLs were grown on (0001) sapphire substrates by molecular beam epitaxy using a GaN buffer layer. The thickness of the SL constituents is kept constant at 2.5 nm, while the Al composition is varied in the range of 0.08–0.61. Details of the samples preparation and their properties can be found in Refs. [5, 11, 12] and references therein.

The vibrational properties of all films were studied by room-temperature GIRSE in conventional (isotropic) and generalized modifications. The GIRSE measurements were performed on a rotating compensator infrared ellipsometer (J. A. Woollam Co, Inc.) in the spectral range of 350–1500 cm\(^{-1}\) with a spectral resolution of 2 cm\(^{-1}\), and at 60° and 70° angles of incidence. For the \( a \)-plane GaN films the GIRSE spectra at each angle of incidence were taken at different angles \( \phi \) between the plane of incidence and the \( c \)-axes of the films.

![Figure 1](www.pss-a.com) Experimental (dots) and calculated (lines) GIRSE spectra of a 1.5 µm-thick \( a \)-plane GaN film on \( r \)-plane sapphire for different angles \( \phi \) between the plane of incidence and the GaN [0001] direction: (a) \( \Psi_p \), (b) \( \Psi_p \) and (c) \( \Psi_p \). The frequencies of the GaN phonon modes of \( A_i \) and \( E_i \) symmetry are indicated. For the sake of clarity the phonon frequencies are given only for polarization along the [1120] direction.
4 Results

4.1 a-plane GaN films: IR anisotropy, phonon splitting and phonon deformation potentials

Experimental and best-fit model calculated $V'$ spectra of a 1.5 µm thick MOVPE $a$-plane GaN layer on $r$-plane sapphire are shown as an example in Fig. 1. The coupling between $p$- and $s$-polarized light, sensed by the off-diagonal elements is small at $\varphi = 0^\circ$ and minimal at $\varphi = 90^\circ$ (Fig. 1(b) and (c)). A noticeable conversion of $p$-($s$-) to $s$-($p$-)polarized light related to the GaN film is observed in the GIRS spectra for intermediate $\varphi$, particularly near frequency regions of resonant excitation of TO or LO phonons. It can be seen that the low-frequency edge of the GaN reststrahlen band moves from $E_i$(TO) to $A_i$(TO) when the azimuth angle, $\varphi$, between the plane of incidence and the GaN c-axis increases from $0^\circ$ to $90^\circ$ (Fig. 1(a)). The $E_i$(TO) and $A_i$(TO) are excited resonantly depending on $\varphi$, particularly near $\varphi = 90^\circ$, which can be related to a material or isotropically strained $c$-plane heteroepitaxial layers [6, 15] is lifted. This subtle anisotropy of the DF in the $x,y$-plane directly reflects the differences in the $E_i$ frequencies for the two main basal plane polarizations (Table 1). The $E_i$(TO) and $E_i$(LO) appear as strong peaks in the imaginary part of $\varepsilon_i$ and $\varepsilon_s$, respectively, while the $E_i$(TO) and $E_i$(LO) in the respective dielectric loss function along the two directions, Im ($-1/\varepsilon_i$) and Im ($-1/\varepsilon_s$), respectively (Fig. 2(a)). The $E_i$ phonon splittings indicate that the strain components along the two basal plane directions are different (see Eq. (2) and Refs. [8, 14]). The presence of anisotropic distortion of the basal plane of $a$-plane wurzite layers causes spectral narrowing differences between the imaginary parts within the phonon mode resonance region (dichroism). A comparison with respect to the strain-free phonon frequencies [6, 18] implies tensile strain along the [1120] direction, which is the growth direction, and compression along the [1000], as schematically shown in Fig. 2(b). Such anisotropic distortion of the basal plane is expected from the differences in thermal expansion coefficients and lattice mismatches between GaN and sapphire along the two directions and has been confirmed by high-resolution X-ray diffraction (HRXRD) studies [5, 6]. It is worth noting that similar optical dichroism caused by anisotropic strain should also be detected for $c$-plane group-III nitride films grown on low-symmetry cut sapphire and SiC substrates. Indeed, we have observed phonon splittings for polar $c$-plane GaN films grown on $a$-plane sapphire, revealing anisotropic compression of the basal plane [5, 19, 20].

It can be seen from Table 1 that the broadening parameters of the $E_i$ phonons polarized along the [1120] and [1000] directions also show a subtle difference. The broadening parameters of the $E_i$ phonons are smaller compared to those of the $E'_i$ phonons, which can be related to a smaller tensile strain (in absolute magnitude) along the [1120] direction than the compressive strain (in absolute magnitude) along [1000] direction [5, 19]. The high-frequency dielectric constant also shows a subtle anisotropy in the $x,y$-plane, which may be related to strain-induced anisotropy. The in-plane dielectric constants are both smaller than $\varepsilon_{xxx}$ along the [0001] direction, deter-

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<td>$2.74 \pm 0.01$</td>
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Table 1 Best-fit high-frequency limit of the DF, $\varepsilon_{xx}$, TO and LO phonon frequencies: $\omega_{TO}$ and $\omega_{LO}$ and broadening parameters, $\gamma$, for different polarizations $E_j || x, y, z$. 

Figure 2 (online colour at: www.pss-a.com) (a) Real and imaginary parts of the DFs, $\varepsilon_i$ and imaginary part of the dielectric loss functions, $-1/\varepsilon_i$, for out-of-plane $x$ and in-plane $z$-directions of an 1.5 µm thick $a$-plane GaN film grown on $r$-plane sapphire. For clarity, the functions for directions $y$ are given through the differences between those for directions $x ||$ GaN [1120] and $y ||$ GaN [1000]. (b) Schematic drawing of the distortion of the GaN basal plane of $a$-plane GaN films under anisotropic strain. The undistorted basal planes are indicated by dashed lines.

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mined to be 5.14 ± 0.01 in good agreement with previous theoretical and experimental findings for GaN [8, 15].

The splitting of the $E_2^\prime(\text{TO})$ phonons is also observed in the Raman spectra of the $a$-plane GaN films. Figure 3 shows Raman spectra from an $a$-plane film in two back-scattering configurations: $x(y, y + z)\overline{\Gamma}$ and $y(x, x + z)\overline{\Gamma}$ with $x$ parallel to [1\,1\,\overline{2}0], $y$ parallel to the [1\,\overline{1}\,00] and $z$ parallel to the [0\,0\,01] directions. In the two configurations there was no polarization detection, which allows the simultaneous detection of the $A_1(\text{TO}), E_1(\text{TO})$ and $E_2$ phonon modes. For phonon propagation along the $x$-axis $A_1(\text{TO}), E_1(\text{TO})$ ($yz$ component of the polarizability tensor) and $E_2$ ($yx$ component of the polarizability tensor) phonon modes are observed. On the other hand, when the light propagates along the $y$-axis, $A_1(\text{TO})$ ($xx$ component of the polarizability tensor), $E_1(\text{TO})$ ($xz$ component of the polarizability tensor), and $E_2$ ($xx$ component of the polarizability tensor) are observed. It is seen from Fig. 3 that for the two configurations, $E_1(\text{TO})$ and $E_2(\text{TO})$ appear at different frequency positions in agreement with the GIRSE results. A similar splitting is also observed for the $E_2$ modes (Fig. 3) in agreement with theoretical predictions for $\varepsilon_{xx} \neq \varepsilon_{yy}$ (see Eq. (2)). At the same time, the $A_1(\text{TO})$ phonon does not split (Fig. 3) in agreement with theory that predicts shift of the $A_1$ phonons only with respect to the strain-free frequency (see Eq. (1)) [8, 14].

The spectral dichroism of the $a$-plane oriented GaN films can be used to determine the strain components if the phonon deformation potentials are known. A correlation of the observed phonon shifts and splittings with respect to the strain-free frequencies with anisotropic strain components, independently determined by HRXRD, allows determination of the phonon deformation potentials, $a$, $b$ and $c$ (see Eqs. (1) and (2)) [5, 6, 19, 20]. This is demonstrated for the $A_1(\text{TO})$ phonon in Fig. 4 which shows the dependence of the $A_1(\text{TO})$ frequency on the in-plane strain components, $\varepsilon_{xx}$ and $\varepsilon_{yx}$ using phonon deformation potentials $a = -664$ cm$^{-1}$ and $b = -1182$ cm$^{-1}$, and strain-free frequency $\omega_0 = 531.2$ cm$^{-1}$ as determined by GIRSE [5, 6]. The squares show the calculated frequencies using the measured $\varepsilon_{xx}$ and $\varepsilon_{yx}$ and the respective labels give the frequency values as determined by GIRSE analysis.

measured $\varepsilon_{xx}$ and $\varepsilon_{yx}$ and the respective labels give the frequency values as determined from the GIRSE analysis. A more detailed description of the determination of the GaN anisotropic and isotropic phonon deformation potentials can be found in Refs. [5, 6, 19].

4.2 Al(Ga)N/GaN superlattices: strain and composition The Al(Ga)N/GaN SLs were grown along the $c$-direction on (0001) sapphire and therefore experience biaxial isotropic strain [11, 12]. The out-of-plane and in-plane strain components are related within the framework of linear elasticity theory (if the piezoelectric and pyroelectric effects are neglected) by:

$$\varepsilon_{zz} = \frac{2C_{13}}{C_{33}} \varepsilon_{xx},$$

where $C_{ij}$ are the elastic stiffness constants. In the case of biaxial isotropic strain, $\varepsilon_{xx} = \varepsilon_{yy}$ and thus the in-plane MDF has been treated isotropically: $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon$ [11, 12]. The $A_1(\text{TO})$ phonon mode is not accessible via GIRSE on $c$-plane oriented films because there is no sensitivity to the TO resonance with polarization vector parallel to the sample normal [15].

Figures 5 and 6 show experimental and calculated $\gamma$ spectra for the AlN/GaN and Al$_{1-x}$Ga$_x$N/GaN SLs, respectively. For all SLs the experimental and best-fit calculated data agree excellently with each other. We have identified from the GIRSE data modeling the following phonon modes originating from the SLs: (i) localized $E_1(\text{LO})$ and $A_1(\text{LO})$ in both the Al(Ga)N and GaN sublayers, (ii) delocalized $E_1(\text{LO})$ phonon, (iii) delocalized modes with $E_1(\text{TO})$ symmetry at 593 cm$^{-1}$ and 625 cm$^{-1}$ in the case of AlN/GaN SLs, and (iv) a low-polarity mode around...
Figure 5 (online colour at: www.pss-a.com) Experimental (dots) and calculated (solid lines) GIRSE $\Psi$ spectra for the AlN/GaN SLs at 70° angle of incidence. The phonon modes originating from the SL constituents are indicated. Two delocalized modes, $A$ and $B$, not predicted by the theory are also indicated.

660 cm$^{-1}$ localized in the AlGaN sublayers and a delocalized mode with $E_1$(LO) symmetry around 595–620 cm$^{-1}$. The first two groups of phonon modes are expected to occur according to the theoretical predictions, while the delocalized modes from the third and fourth group have not been predicted [10]. The SL phonon modes that can be related to resonance structures in $\Psi$ are indicated in Figs. 5 and 6.

In general, the magnitudes of the phonon frequencies in a SL are expected to depend mainly on the relative content of the different nitrides in the SL and the strain. For the AlN/GaN SLs only the strain effect is relevant, since the well-to-barrier ratio is kept constant when the SL period is changed. The dependencies of the SL mode frequencies on the experimentally determined in-plane strain in the respective sublayer for the localized modes, and on the weighted in-plane strain in the case of delocalized modes, have been analyzed for the AlN/GaN SLs [11]. As a result, the strain-free values of the SL modes and respective frequency shifts are determined. Figure 7 present the shifts of the identified localized modes versus the in-plane strain in the GaN sublayers. In addition to the experimental data theoretical estimations for the frequency shifts without accounting for the polarization fields (Eq. (9)) and accounting for the polarization fields [11] are also presented in Fig. 7 for comparison.

The frequency shifts of the localized modes within the GaN SL sublayers of the AlN/GaN SLs show a linear dependence on the in-plane strain, and a good agreement with the theoretically estimated shifts (see Fig. 7). Hence, the frequencies of GaN localized phonons may serve as a probe of strain in the well sublayers. The effect of the polarization fields amounts to 0.6–1 cm$^{-1}$, depending on the particular mode and sublayer thickness, most often being

Figure 6 (online colour at: www.pss-a.com) Experimental (dots) and calculated (solid lines) GIRSE $\Psi$ spectra of the AlGaN/GaN SLs studied, at 70° angle of incidence. The Al composition is specified above the respective spectra. The phonon modes originating from the SL constituents are indicated with arrows. Two SL modes, $A$ and $B$, not predicted by the theory are also indicated.
Frequency shifts of the localized phonon modes in the GaN sublayers of the AlN/GaN SLs versus the in-plane strain, $\varepsilon_{xx}$: (a) $E_1$(TO) and (b) $A_1$(LO). The experimental shifts are indicated by full squares and the fits to the experimental points are given by dashed lines. The theoretical estimations for the respective frequency shifts are given with hollow squares when no polarization fields effect is considered, and with hollow triangles when the latter effect is accounted for.

Within the errors of the experimentally determined shifts, but nonetheless needing to be accounted for. We have determined the following strain free-frequencies for the GaN localized modes: $559.5 \pm 0.2 \text{ cm}^{-1}$ for the $E_1$(TO) and $741.5 \pm 0.8 \text{ cm}^{-1}$ for the $A_1$(LO). These values appear slightly blue-shifted with respect to the strain-free frequencies of the respective modes in bulk GaN [18] ($558.2 \text{ cm}^{-1}$ and $736.5 \text{ cm}^{-1}$, respectively), which might be related to the presence of interface disorder or possible delocalization effects.

In contrast to the GaN localized modes, the strain-free frequencies of phonons localized in the AlN sublayers of the AlN/GaN SLs have much higher frequencies than the strain-free values of the respective modes reported for bulk AlN: $727.6 \pm 18 \text{ cm}^{-1}$ for the $E_1$(TO) and $941 \pm 48 \text{ cm}^{-1}$ for the $A_1$(LO), compared to $669 \text{ cm}^{-1}$ and $890 \text{ cm}^{-1}$ for bulk AlN [21], respectively. Accordingly, the AlN localized modes show very large shifts compared to the estimations using the elasticity theory and accounting for the polarization effects [11] and therefore complicates their use for strain assessment in the barrier sublayers. Note, however, that it is more important to assess strain in the GaN sublayers, where direct and assumption-free strain determination from HRXRD is not possible. More experimental and theoretical work is required in order to distinguish whether the observed large deviations of the AlN SL phonon frequencies are intrinsic or related to the uncertainties in the phonon deformation potentials of AlN [22–24], or to local distortion of the coherence of the SL structure.

The frequency of the delocalized $E_1$(LO) shows a blue-shift with decreasing the weighted tensile in-plane strain in the AlN/GaN SLs [11]. The linear fit to the experimental frequencies gives a strain-free value of $925.2 \pm 8.4 \text{ cm}^{-1}$ close to the AlN $E_1$(LO) frequency of $911 \text{ cm}^{-1}$ [21] and much higher than the estimated frequency of the “normal” $E_1$(LO) line of around $796 \text{ cm}^{-1}$ [11]. Such a deviation may be explained by reduced delocalization of the mode leading to predominant localization in the AlN sublayers. In addition the delocalized LO phonons are sensitive to free-carriers in the GaN wells, caused by the presence of 2DEG when the Fermi level is pinned at the surface [11]. The free-electron densities in the SL GaN sublayers are found from GIRSE data modeling to be on the order of or higher than $10^{18} \text{ cm}^{-3}$ [11]. At such concentrations the plasma modes will couple to the LO lattice modes and will form the so-called coupled LO-plasmon-phonon modes. This results in a shift of the zeros of the GaN sublayer DF to higher frequencies and thus the delocalized SL $E_1$(LO) phonon may appear at higher frequencies compared to the non-coupled delocalized mode. Hence, the degree of delocalization provides a means to assess the effect of polarization fields and in combination with strain determination may be used for...
estimation of the spontaneous polarizations in the SL constituents.

Figures 8 show the AlGaN DF for the AlGaN/GaN SLs: (a) Im($\varepsilon_2$), where the $E_2$(TO) phonons appear as strong peaks, and (b) the imaginary part of dielectric loss function, Im($-1/\varepsilon_0$), where the $A_1$(LO) phonon appears as a strong peak. The $E_1$(TO) mode localized in the AlGaN barriers shows a two-mode behavior [Fig. 8(a)], while the $A_1$(LO) exhibits one-mode behavior [Fig. 8(b)] as in bulk alloys. The phonon frequencies change with changing Al composition as a result of the combined effects of strain and composition (the well and barrier thicknesses are kept constant).

The phonon frequencies of the localized modes have been corrected for the effect of strain using the experimentally determined in-plane strains and accounting for the effect of the polarizations fields [11, 12]. The analysis of the strain-corrected phonon frequencies with changing Al composition show that the GaN-like $E_1$(TO) mode experiences a linear blue-shift with increasing Al composition [Fig. 8(a)]. In contrast, the AlN-like $E_1$(TO) mode seems to be insensitive to the Al composition in the range studied in line with previous theoretical predictions for bulk alloys [25]. The AlGaN $A_1$(LO) frequency increases with increasing Al composition [Fig. 8(b)] showing a small negative bowing. The phonon frequency of the localized modes as a function of the Al content can be approximated by the following equations in cm$^{-1}$:

$$\omega_{E_1^{\text{GN}}}(\text{TO}) = 560.5 + 84.8x,$$
$$\omega_{E_1^{\text{GN}}}(\text{LO}) = 635.5,$$
$$\omega_{A_1^{\text{GN}}}(\text{LO}) = 748.3 + 139.4x - bx(1-x), \quad b = -53.5.$$

Therefore, both GaN-like $E_1$(TO) and $A_1$(LO) phonon frequencies show a high sensitivity to the composition and can be used to measure the AlN content in the AlGaN barrier layers.

The GIRSE findings are corroborated and complemented with micro-Raman scattering experiments and further details on the SL phonon mode behavior can be found in Refs. [11, 12].

5 Conclusion It has been demonstrated that GIRSE gives an opportunity to study fascinating and unexplored physical phenomena in an important class of semiconductor uniaxial material, group-III nitrides. The application of GIRSE to non-polar group-III nitrides, e.g., $a$-plane GaN films, reveals the complete dielectric tensor anisotropy of the materials. GIRSE is able to detect spectrally narrow dichroism caused by anisotropic strain, which allows identification of subtle phonon shifts and splittings. GIRSE was shown to be a vital tool in determination of phonon deformation potentials in GaN, which enables the use of phonon frequencies as gauge of lattice deformation. Further, application of GIRSE to the studies of Al(Ga)N/GaN SLs allows identification of their phonon modes, providing means of precise control and metrology of individual layers in complex device heterostructures, namely estimation of strain, polarization doping, and composition.

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References


