Angular-dependent Raman study of $a$- and $s$-plane InN

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Abstract

Angular-dependent polarized Raman spectroscopy was utilized to study nonpolar $α$-plane (1 1 2 0) and semipolar $s$-plane (1 0 1 1) InN epilayers. The intensity dependence of the Raman peaks assigned to the vibrational modes $A_1$(TO), $E_1$(TO) and $E_2^\text{b}$ on the angle $ψ$, that corresponds to rotation around the growth axis, is very well reproduced by using expressions taking into account the corresponding Raman tensors and the experimental geometry, providing thus a reliable technique towards assessing the sample quality. The $s$- and $a$-plane InN epilayers grown on nitridated $r$-plane sapphire ($\text{Al}_2\text{O}_3$), exhibit good crystalline quality as deduced from the excellent fitting of the experimental angle-dependent peak intensities to the theoretical expressions as well as from the small width of the Raman peaks. On the contrary, in the case of the $s$-plane epilayer grown on non-nitridated $r$-plane sapphire, fitting of the angular dependence is much worse and can be modeled only by considering the presence of two structural modifications, rotated so as their $c$-axes are almost

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perpendicular to each other. Although the presence of the second variant is verified by transmission electron and atomic force microscopies, angular dependent Raman spectroscopy offers a non-destructive and quick way for its quantification. Rapid thermal annealing of this sample did not affect the angular dependence of the peak intensities. The shift of the $E_1$(TO) and $E_2^h$ Raman peaks was used for the estimation of the strain state of the samples.

**Keywords:** InN; Raman; semipolar; nonpolar; polarization dependence; strain

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I. Introduction

The re-evaluation of the fundamental energy gap of InN in the infrared spectral region along with its high electron mobility values attracted a lot of interest for its use in the fabrication of opto- and micro-electronic devices, high efficiency solar cells, optical coatings and various types of sensors.\(^1\)\(^-\)\(^4\) Furthermore, alloying of InN with GaN and/or AlN, extends the spectral range of emitting devices into the visible regime of the spectrum. However, the growth of group-III nitrides in the common (0001) polar orientation, results in heterostructures with large internal electric fields which deteriorate the efficiency of light emitting devices.\(^5\) To overcome this drawback, growth in nonpolar directions that would result in improved quantum efficiency of light emitting devices has been proposed.\(^6\) \(a\)-plane InN films were grown on \(r\)-plane sapphire substrates by plasma-assisted molecular beam epitaxy (PAMBE) after a substrate nitridation process.\(^7\) Furthermore, the growth of a low-temperature (LT) InN buffer layer prior to the epilayer growth has resulted in the improvement of the surface quality of the \(a\)-plane InN layers.\(^8\) The use of a thin (35 nm) LT \(a\)-plane GaN nucleation layer has resulted to \(a\)-plane InN films with isotropic surface characteristics, while strong anisotropy was observed for InN growth on 1 \(\mu\)m-thick \(a\)-plane GaN buffer layers.\(^9\) The structural quality of such films improved with increasing film thickness, as it was deduced from the width of the X-ray diffraction (XRD) rocking curves and the photoluminescence intensity.\(^9\) Both the type of nucleation layer and the conditions for the sapphire substrate nitridation process appear to play an important role in the orientation of the InN epilayers determining their semipolar character.\(^10,\)\(^11\)

In semipolar orientations the \(c\)-axis is inclined relative to the growth direction whereas in nonpolar ones it lies in the growth surface.\(^12\) Except from growth of semipolar InN layers on sapphire substrates\(^11,\)\(^-\)\(^14\) such layers were also grown on GaAs (110)\(^15\) and yttria stabilized zirconia.\(^16\) Specific features of semipolar InGaN/GaN structures, as for example lower polarization charge at the interface, are considered as beneficial for improving the optical and transport properties of quantum-well based light emitting devices.\(^5\) Towards the fabrication of long-wavelength optoelectronic devices, InGaN/AlGaN/GaN (\(1\overline{2}2\)) heterostructures\(^17\) and semipolar InGaN/GaN
quantum dot superlattices\textsuperscript{18,19} were grown on GaN (11\overline{2}2)/m-sapphire templates. However, semipolar InN layers are still of inferior crystalline quality compared to the polar counterparts. A common extended defect observed in s-plane epilayers is the coexistence of two structural modifications with domains rotated by approximately 90° with respect to each other.\textsuperscript{11,12,14,20}

Raman spectroscopy is a well-established, non destructive, technique for assessing the crystalline quality and strain state of semiconductors. Polarized or angular dependent Raman spectroscopy can also detect strain-induced unit cell distortions. For example, uniaxial or biaxial strain distributions in silicon-on-insulator microstructures has been found to result in the appearance of Raman peaks that are inactive in strain-free Si, due to the reduction of crystal symmetry.\textsuperscript{21} Regarding the group-III nitrides that crystallize in the wurtzite structure, their Raman spectra exhibit strong angular dependence on the exciting laser polarization.\textsuperscript{22} Hence, polarized Raman spectroscopy has been broadly applied to reveal unknown crystallographic orientations of wurtzite GaN\textsuperscript{23} as well as for the study of group-III nitride nanorods and nanowires.\textsuperscript{24-26} Recently, deviations from the expected angular dependence of the Raman peak intensities in anisotropically strained α-plane GaN epilayers have been attributed to the presence of an orthorhombic distortion of the hexagonal unit cell caused by the strain anisotropy.\textsuperscript{27}

In this work, we study the angular dependence of the Raman peak intensities of the $A_1$(TO), $E_1$(TO) and $E_2^\text{h}$ vibrational modes in α- and s-plane InN epilayers grown by PAMBE on r-plane (1\overline{1}02) Al\textsubscript{2}O\textsubscript{3}. In the former case, where the $c$-axis lies on the sample surface, some peaks assigned to modes with specific symmetry were suppressed for certain sample orientations, facilitating the estimation of the corresponding Raman tensor elements. These tensor elements were then used for the study of the angular dependence of the Raman peak intensities in s-plane epilayers, where, due to the oblique orientation of the $c$-axis, the theoretically predicted expressions are more complicated. The effects of substrate nitridation on the $s$-plane InN growth and of ex-situ annealing treatments of the grown sample were also considered. Finally, information on the strain state of the samples was obtained from the shift of the $E_1$(TO) and $E_2^\text{h}$ Raman peaks.
II. Growth conditions and experimental details

Nonpolar (a-plane) and semipolar (s-plane) InN layers grown on r-plane (1T02) Al$_2$O$_3$ substrates by PAMBE$^{12,14}$ were investigated. Details for the PAMBE system and the conditions for InN have been described previously.$^{9,28,29}$ In the case of the s-plane layers, the effect of substrate nitridation during growth and a post-growth rapid thermal annealing (RTA) treatment were also studied. The RTA treatment consisted of heating for 1 sec at 650°C under N$_2$ atmosphere. In Table I the sample names along with the corresponding growth conditions are listed. The surface morphology of the samples was characterized by atomic force microscopy (AFM). Cross sectional transmission electron microscopy (TEM) observations, using a 200 kV LaB$_6$ JEOL 2011 microscope, were employed for the microstructural characterization of the samples.

The Raman spectra were recorded at room temperature in the backscattering geometry using a triple grating DILOR XY system equipped with a microscope and a liquid nitrogen cooled charge coupled device detector. The spectral resolution of the system was 2 cm$^{-1}$ and the beam diameter was approximately 1 μm. The Raman spectra were excited using the 514.5 nm line of an Ar$^+$ laser, whereas a Ne lamp was used for the Raman frequency calibration. The laser power on the sample surface was 5 mW. To exploit the angular dependence of the Raman peak intensities, we resorted to the experiment geometry shown in Fig. 1. OXYZ and Oxyz is the lab- and sample-fixed coordinate system, respectively. In the case of the α-plane (1120) layer, the c-axis lies on the growth plane, whereas in the s-plane (10T1) ones, the s-axis points in-between the m- and c- axes, forming an angle of 62° to the c-axis. The Raman spectra were recorded for two different electric field polarizations (along OX and OY) of the incident laser light propagating along OZ. The sample was rotated around the OZ-axis, thus varying the angle $\psi$ between the projection of the c-axis on the sample surface and the polarization of the incident laser beam.
III. Results and discussion

III.1. Symmetry considerations

The Raman spectra of crystalline semiconductors that crystallize in the wurtzite structure are sensitive to the orientation of the sample because the phonon modes that correspond to different symmetries of vibration are characterized by irreducible representations leading to different selection rules.\textsuperscript{30} Group theory analysis for the \(C_{6v}^4\) (P6\(_3\)mc) space group, where wurtzite InN belongs, predicts six vibrational optical modes at the centre of the Brillouin zone, \(A_1+2B_1+E_1+2E_2\). The \(A_1\), \(E_1\) and the two \(E_2\) modes are Raman active, whereas the \(B_1\) modes are silent. One of the \(E_2\) modes, the \(E_2^L\), appears in the low frequency range and is mainly determined by vibrations of the heavier atoms i.e. In, whereas the second, denoted as \(E_2^b\), appears in the high frequency range and is mainly determined by vibrations of the N atoms. The \(A_1\) and \(E_1\) modes are further split into longitudinal optical (LO) and transverse optical (TO) due to their polar character.\textsuperscript{31} The LO-TO splitting is approximately 5.5 times higher compared to the \(A_1-E_1\) splitting, indicating that the long range electrostatic field dominates over the vibrational force-constant anisotropy.\textsuperscript{32} The vibration direction of the atoms in the InN lattice is depicted in Fig. 1(f). For propagation direction along \(z\), which is taken parallel to the \(c\)-axis, the \(A_1\) is a LO mode, whereas for propagation direction along \(x\) or \(y\), the \(A_1\) is of transverse and the \(E_1\) of longitudinal and/or transverse character. For propagation direction in-between \(z\) and \(x\) or \(y\), both the TO and LO modes might appear in the spectrum.\textsuperscript{33} This is the case of the \(s\)-plane layers indicated in Fig. 1(e), where the phonon propagation direction, \(\mathbf{q}\), that is along \(Z\) in the backscattering geometry, lies in the \(z-y\) plane. Thus, peaks that correspond to both LO and TO modes, which might be a mixture of \(A_1\) and \(E_1\) symmetry, are expected in the Raman spectra. As far as the TO modes are concerned, one \(E_1\)(TO) mode and one quasi-mode [denoted as \(Q\)(TO)] are expected in the \(s\)-plane sample.\textsuperscript{34,35} The intensity of the Raman peaks depends strongly on the polarization direction of the incident and scattered light with respect to the principal axes of the investigated crystal. The Raman scattering efficiency \(S\), is described by the expression:\textsuperscript{34}

\[
S = \left\{ \sum_{\rho \sigma \tau \in \text{xyz}} e_{\rho}^{\sigma} R_{\rho \sigma}^{\tau} (\alpha \xi^{\tau} + \beta \bar{q}^{\tau}) e_{\tau}^{\rho} \right\}^2
\]  

(1)
where \( e_i' \) and \( e_s' \) are the components of the polarization unit vector of the incident and scattered light, respectively, \( R_{ij} \) stand for the Raman tensor components, whereas \( \xi \) and \( \hat{q} \) are vectors in the direction of phonon polarization (mechanical stress) and phonon propagation direction, respectively, and \( \alpha \) and \( \beta \) are constants. In uniaxial crystals, \( \beta \) is always equal to zero for pure transverse and non-polar modes. Therefore, in the following the simplified expression for the intensity, \( I \), of a given Raman mode is used:

\[
I = |\hat{e}_i R' \hat{e}_s|^{2}
\]

where \( R' \) is the Raman tensor after proper rotation for consistency with the growth orientation of the sample and the experimental geometry, whereas \( \hat{e}_i \) and \( \hat{e}_s \) are the unit polarization vectors of the incident and scattered light, respectively. The Raman spectra were recorded for \( \hat{e}_i \parallel OX \) and \( \hat{e}_i \parallel OY \) while the scattered light was intentionally non-polarized. Therefore, the Raman peak intensities contain contributions from two polarization geometries, one along the \( OX \) and one along \( OY \) directions, with weighting factors 0.15 and 0.85, respectively that reflect the polarization transfer function of the optical system used. The analytic expressions of the dependence of the Raman peak intensity on the angles \( \theta, \phi \) and \( \psi \) are derived in the Appendix. We point out that while the intensities of the individual \( E_1 \) peak contributions, i.e. \( E_1(x) \) and \( E_1(y) \), depend on the angle \( \phi \), their sum that provides the total \( E_1 \) intensity does not show any \( \phi \)-dependence. We remind that the \( O_x \) axis is considered along the 6-fold symmetry axis, i.e. \( O_x \parallel [0001] \) and the \( O_y \) and \( O_x \) axes along the \([10\bar{1}0]\) (\( m \)-axis) and \([\bar{1}2\bar{1}0]\) (\( a \)-axis) direction, respectively (Fig. 1). In the case of the \( \alpha \)-plane sample the \( c \)-axis lies on the sample surface, \( \text{viz.} \ \theta=\pi/2 \) and \( \phi=0^\circ \).

For the \( s \)-plane samples, the growth plane is \( [10\bar{1}1] \), and the corresponding normal vector \([10\bar{1}(1/\Lambda^2)]\), where \( \Lambda = \sqrt{2/3} \cdot \frac{c}{a} \), coincides with the lab-fixed \( OZ \) axis.

Taking \( a \) and \( c \) equal to 0.3535 and 0.5699 nm, respectively, the angle between the \( c \)- and \( s \)-axes is 61.8°. Therefore, the successive rotations that result in coincidence of the wurtzite \( Oxyz \) system with the lab-fixed \( OXYZ \) system are: i) a rotation around the
z-axis by $\phi = 90^\circ$ so that the $x$-axis coincides with the $y$-axis and (ii) a rotation around the $y$-axis by $\theta = 61.8^\circ$.

Selected characteristic sample orientations and experimental geometries along with Raman peak intensities are tabulated in Table II. Generally, in $c$-plane samples only the $E_2$ and $A_1$(LO) peaks are observed and they exhibit a constant intensity upon $\psi$ rotation. Contrary to the $c$-plane samples, in the $a$-plane ones, the $A_1$(TO), $E_1$(TO), $E_2^b$ and $E_1$(LO) modes can be observed and their Raman peak intensities exhibit strong angular dependence. The variation of the polarization of the incident and scattered light would result in suppression of some contributions of the Raman tensors characterized by degeneracy allowing for the study of strain anisotropy. For the $s$-plane samples, due to the oblique orientation of the $c$-axis, full peak suppression hardly occurs. It should be pointed out that equations A6-A8 can be also used as an alternative method to microscopy for the determination of the orientation of the $c$-axis on the sample by adding a parameter $\Delta \psi$ in the angle $\psi$ that could be properly iterated.

As mentioned above, when the phonon propagation direction is not along a high symmetry axis (i.e. parallel to $x,y,z$) mixing of the $A_1$ and $E_1$ modes occurs, and quasi modes of mixed symmetry are observed in the Raman spectra. In the case of the $s$-plane samples, the laser beam is impinging at an angle of $61.8^\circ$ with respect to the $c$-axis and normal to the $a$-axis that lies on the sample surface. Thus, the phonon propagation direction that lies along the $OZ$ axis maintains the same angle with the $c$-axis upon $\psi$-rotation and it is normal to the $a$-axis resulting in the appearance of two TO peaks that correspond to a $E_1$(TO) and a $Q$(TO) mode (Fig. 3). For the $A_1$(LO) and $E_1$(LO) modes, it can not be unambiguously deduced, because of their small frequency difference ($\sim 7$ cm$^{-1}$) and relative broad shape, if the structure around 595 cm$^{-1}$ is a single peak associated with a quasi-mode, $Q$(LO), or it consists of two close-lying separate peaks. In the former case, the frequency of the $Q$(LO) mode, $\omega_{Q(LO)}$, would be given by:

$$\omega_{Q(LO)} = \sqrt{\omega_{A_1(LO)}^2 \cos^2 \theta + \omega_{E_1(LO)}^2 \sin^2 \theta} = 591.5 \text{ cm}^{-1}$$ (3)

where $\theta = 61.8^\circ$ and $\omega_{A_1(LO)}$ and $\omega_{E_1(LO)}$ the corresponding frequencies for the $A_1$(LO) and $E_1$(LO) modes (see Table II). Due to the difficulty in an unambiguous
clarification of the LO band origin, in the following we restrict the study of the angular dependence of the Raman peak intensities to that of the TO modes. An additional reason for not considering the LO modes, is the complexity arising from the electro-optical terms, resulting from electron-lattice interactions, that should be also taken into account.\textsuperscript{34,35,43-45} In that case the angular dependence of the LO peak intensities deviate from the scattering efficiencies described in the Appendix, due to the long-range electric fields produced by the polar lattice vibrations ($\beta\neq0$ in Eq. 1). These fields give rise to electron-lattice interactions that vary with phonon wave vector due to the variation of the field strength.

III.2. $\psi$-dependence of the Raman peak intensities

Typical Raman spectra recorded at selected $\psi$ angles for $\hat{e}_i || OX$ and $\hat{e}_f || OY$ polarizations are shown in Figs. 2 and 3 for samples grown on nitridated substrates, AN ($a$-plane) and SN ($s$-plane), respectively. The low frequency part of the spectrum is dominated by Rayleigh scattering and thus only the peaks appearing at wavenumbers higher than 400 cm$^{-1}$ are shown and discussed in the following. The peaks assigned to $A_1$(TO), $E_1$(TO), $E_2^h$ and $E_{1}(LO)$ modes for the $a$-plane sample and to $E_1$(TO), Q(TO) and Q(LO) for the $s$-plane sample are well resolved. In both cases, the relative intensities of the Raman peaks vary upon changing the angle $\psi$. According to Table II, for the $a$-plane samples, complete suppression of the $E_2^h$ mode is expected for incident light polarized along X (Y) and for $\psi=0$ and 180° ($\psi=90°$ and 270°). This behavior is observed in Fig. 2(b) (Fig. 2(a)). Correspondingly, the $E_1$(TO) peak should cease for parallel ($Z(XX)\bar{Z}$ or $Z(YY)\bar{Z}$) polarization and $\psi=0, 90, 180°$. Finally, the $A_1$(TO) peak is expected to cease for cross ($Z(XY)\bar{Z}$ or $Z(YX)\bar{Z}$) polarization and $\psi=0, 90, 180°$. Taking into account that the scattered radiation is predominantly polarized along Y, such minimizations in the $E_1$(TO) and $A_1$(TO) intensities observed in Fig. 2(b) and 2(a), respectively can be explained.

To obtain quantitative information from the $\psi$-dependence of the Raman peak intensities, they were fitted to Lorentzian lineshapes at each angle $\psi$. The full width at half maximum (FWHM) of the $A_1$(TO), $E_1$(TO), $E_2^h$ peaks is: 7.8±0.3(8.6±0.5),
7.9±0.3(8.1±0.4) and 9.0±0.4(8.0±0.4) cm⁻¹ for the AN (SN) sample. The given values are mean values of those obtained for different sample orientations. The FWHM of the $E_2^\text{b}$ peak for the nonpolar and semipolar layers is much higher compared to the corresponding width in good quality $c$-plane epilayers⁴⁶ that is consistent with the higher concentration of extended defects in nonpolar and semipolar InN.⁹,¹²

The dependence of the intensity of the Raman peaks $A_1$(TO), $E_1$(TO) and $E_2^\text{b}$ on $\psi$ for the $\alpha$-plane sample (AN) is illustrated in polar graphs in Fig. 4. The intensity of each peak was normalized to its maximum. The experimental values (data points in Fig. 4) were fitted (solid lines) using Eqs. A6-A8 considering that $\theta = \pi/2$ and $\phi = 0$. The fitting provides only the modulus of the ratio $|a/b|$ of the Raman tensor elements. This ratio, which is a measure of the polarizability anisotropy, is found equal to 0.62 for the InN structure. The good fitting quality of the theoretical expressions to the $\psi$-dependence of the Raman peak intensities reveals the absence of misoriented regions in the AN sample. Furthermore, any significant orthorhombic distortion of the hexagonal unit cell causing different strain values in the basal plane along the $a$ and $m$ axes has to be excluded, since in such a case, faint polarization dependence of the $E_2^\text{b}$ peak would have been observed, like in anisotropically strained $a$-plane GaN.²⁷

Growth of nitrides in nonpolar orientations results in anisotropic characteristics as for example in the surface morphology, the FWHM of the XRD rocking curves and the strain.⁹,²⁰,⁴⁷ However, such anisotropic characteristics, that were attributed to the small difference in the diffusivity of In and N adatoms on the $a$-plane surface along the $c$- and $m$- axis, were not observed in thick InN layers grown on GaN nucleation layers. Thus, the absence of orthorhombic distortion could be also attributed to the large sample thickness⁹ and/or the high concentration of threading dislocations observed by TEM.¹¹

The $\psi$-dependence of the normalized Raman peak intensities in the case of the $s$-plane samples S and SN, is plotted in Fig. 5. The fitting was performed by using the equations A6-A8 and by setting the values of $a$, $b$, $c$ and $d$ equal to the corresponding ones determined in the case of the $\alpha$-plane sample. As it is evident from Fig. 5, the angular dependence of the Raman peak intensities for the S sample is not
satisfactorily reproduced by the theoretical expression, compared to that of sample SN. Furthermore, RTA of the sample S did not improve the fitting quality of the angular dependence of the peak intensities. This is an indication of a higher content of extended defects and/or the presence of misoriented regions. Indeed, in s-plane InN layers that were grown on non-nitridated sapphire substrates with the use of InN buffer layer, the presence of two structural variants and sphaleritic inclusions, attributed to the high concentration of stacking faults, has been observed.\textsuperscript{11} The inferior crystalline quality of sample S compared to that of the sample SN is also evidenced from the larger width of the Raman peaks. More specifically, the FWHM of the Q(TO), E\textsubscript{1}(TO) and E\textsubscript{2}\textsuperscript{s} peak is 13.2±0.6(14.8±0.6), 10.5±0.5(10.8±0.4) and 9.7±0.3(8.2±0.2) cm\textsuperscript{-1} before (after) annealing, respectively. The RTA-induced decrease in the E\textsubscript{2}\textsuperscript{s} peak FWHM by approximately 15% could be attributed to the reduction of the density of the basal plane stacking faults that is observed by transmission electron microscopy (TEM) measurements.\textsuperscript{14} It should be mentioned that the presence of multiple stacking faults in wurtzite polytypes is structurally equivalent to the inclusion of cubic phase in the samples. The TO and LO phonon modes of the cubic InN phase are expected to appear in the frequency range 470-475 and 586-588 cm\textsuperscript{-1}, respectively.\textsuperscript{48} According to Table II, these values lie in the frequency range of the E\textsubscript{1}(TO) and LO phonon modes of the hexagonal polytype and thus can not be used for the detection of cubic-phase inclusions present in the sample, as in the case of GaN.\textsuperscript{49} Furthermore, neither the angular dependence of the Raman peak intensities can be used for the discrimination of the cubic and hexagonal phases since they differ only in the stacking sequence of the atomic planes along the [111] and [0001] axes, respectively. In the cubic structure, only F\textsubscript{2} Raman modes are allowed which are triply degenerate along the x, y, z axes.\textsuperscript{34} However, in the wurtzite phase the hexagonal crystal field causes splitting of these modes into A\textsubscript{1} and E\textsubscript{1} modes with frequencies similar to that of F\textsubscript{2}. The expected angular dependence of the TO mode of the cubic phase, obtained following the same procedure as in the case of the hexagonal structure, i.e. transforming the triply degenerate Raman tensors\textsuperscript{34} is qualitatively similar to that of the E\textsubscript{1}(TO) of the hexagonal. Another reason for not observing cubic contribution might be their small size that results in strong phonon confinement, held responsible for considerable broadening (and consequently significant suppression), of the corresponding Raman peaks.
The better description of the $\psi$-dependence of the Raman intensities for the SN-, compared to that for S-sample by the theoretical model, has to be ascribed to the effect of nitridation of the Al$_2$O$_3$ substrate. In the case of $s$-plane$^{11,12,14}$ and $m$-plane$^{20}$ epilayers grown on non-nitridated substrates, two structural variants which are rotated by approximately 90° with respect to each other have been previously reported and identified by TEM. The presence of these two variants, or equivalently domains with different orientations of the $c$-axes, could explain the worse angular dependence of the Raman peak intensities of sample S. To verify this effect, we have fitted the corresponding $\psi$-dependence of the Raman intensities by means of a weighted average of two $s$-plane contributions, rotated to each other by $\Delta \psi = 90°$. The obtained fitting curves are plotted as dashed lines in Figs. 5(a) and (b). The better description of the experimental data by the dashed lines is apparent. The best fitting procedure gives an analogy of 65%-35% for the two variants. This analogy was verified using TEM observations. Figure 6(a) illustrates a cross sectional TEM image of sample S viewed along the $[20\overline{2}\overline{1}]_{\text{sapph.}}$ zone axis of sapphire. One variant is projected along $[\overline{1}0\overline{2}0]_{\text{InN}}$ and the other along $[\overline{2}1\overline{1}3]_{\text{lnN}}$. The two variants give distinct contrast since the variant that is viewed along the $[\overline{1}0\overline{2}0]_{\text{lnN}}$ projection direction is distinguished by the characteristic multiple basal stacking faults.$^{14}$ It is seen that both variants exhibit large crystallites reaching up to the top surface of the film. The ratio in the sizes of the crystallites is in good agreement with the Raman fitting. Contrary to the sample S, in the SN, the second variant is mostly confined in small crystallites very close to the interface as indicated in Fig. 6(b). The co-existence of the two variants in the sample S-RTA is verified by the phase-contrast AFM image shown in Fig. 7. Phase-contrast imaging is sensitive to grain boundaries, strain relaxation, defects and any other kind of imperfection that result in energy dissipation during scanning.$^{50,51}$ Overall, although the presence of the two variants in $s$-plane layers can be identified by TEM and/or AFM, angular dependent Raman measurements offer a fast, non-destructive, alternative approach for the estimation of the average percentage of the two variants in the sample volume.

III.3. Strain
Epitaxial layers often exhibit residual strain of thermal origin due to growth conditions that causes shift / splitting of the Raman peaks. Splitting is present in case of anisotropic strain ($\varepsilon_{xx} \neq \varepsilon_{yy}$) due to degeneracy lifting of the two components of the $E_1$ and $E_2^h$ modes (see Raman tensors in the Appendix) and becomes evident for specific incident and scattering light polarizations and sample orientations.\textsuperscript{42} Anisotropic strain along the $x$ and $y$ axes in the basal plane is also expected to result in symmetry reduction.\textsuperscript{27} The frequency shift and/or splitting of the $E_1$(TO) and $E_2^h$ modes is given by the equation:\textsuperscript{30}

$$
\Delta \omega_{E_1} = a_{E_1} (\varepsilon_{xx} + \varepsilon_{yy}) + b_{E_1} \varepsilon_{zz} \pm c_{E_1} \sqrt{(\varepsilon_{xx} - \varepsilon_{yy})^2 + 4\varepsilon_{xy}^2}
$$

where $a_{E_1}$, $b_{E_1}$ and $c_{E_1}$ are the phonon deformation potentials of the corresponding Raman modes. The frequency shifts, $\Delta \omega$, of the $E_1$(TO) and $E_2^h$ Raman peaks in the studied samples are listed in Table III. The shifts were determined relative to the corresponding values for strain-free samples, 477.9 and 491.1 cm$^{-1}$, respectively.\textsuperscript{52,53} It should be noted that for anisotropically strained GaN the corresponding angular dependence dictates the use of a perturbation term with C$_{2v}$ symmetry that accounts for the orthorhombic distortion of the hexagonal unit cell.\textsuperscript{27} However, in the studied layers, the angular dependence of the normalized Raman peak intensities is well reproduced by the model accounting for pure hexagonal phase, indicating the absence of strain anisotropy in our samples, i.e. $\varepsilon_{xx} \approx \varepsilon_{yy}$. Assuming that the [T2T0], [10T0] and [0001] directions of wurtzite InN are parallel to the Ox, Oy and Oz axis respectively (see Fig. 1), in the case of the $\alpha$-plane sample the shear stress and strain components ($i \neq j$) are zero, i.e. $\varepsilon_{xy} \approx 0$. For the $s$-plane samples, S and SN, $\varepsilon_{xy} = \varepsilon_{xz} = 0$ and $\varepsilon_{yz} \neq 0$, according to Funato et al.\textsuperscript{54} and Romanov et al.\textsuperscript{55} Referring to the coordinate system of Fig. 1, the $z$- and $y$-axis point at approximately 62$^\circ$ and 28$^\circ$ to the normal to the surface, respectively, while $x$ is located on the growth plane. The strain state of the samples is estimated using Eq. 4 and the phonon deformation potentials of wurtzite InN are adopted from Ref. 52: $a_{E_1(\text{TO})} = -735$ cm$^{-1}$, $b_{E_1(\text{TO})} = -699$ cm$^{-1}$, $a_{E_2} = -610$ cm$^{-1}$ and $b_{E_2} = -857$ cm$^{-1}$. The obtained strain components values are listed in Table III. Although the error in the determination of the strain can amount up to 40% of the reported values (it is mainly affected by the uncertainty in values of the phonon
deformation potentials), it can be safely concluded that the studied samples experience tensile strain along the $m$- and $a$- axes and compressive strain along the $c$- axis.

IV. Conclusions

Raman spectra of $\alpha$- and $s$-plane InN epilayers were recorded in the backscattering geometry by varying the angle $\psi$ between the projection of the $c$-axis on the surface and the polarization of the incident laser beam. The dependence of the Raman peak intensities of the $E_{1}(TO)$, $A_{1}(TO)$ [or $Q(TO)$] and $E_{2}^{\text{b}}$ vibrational modes on the rotation angle, was investigated. For the $a$- and $s$-plane samples grown on a nitridated sapphire substrate a good agreement between experimental and theoretical dependence of the Raman intensities was observed. From the fitting of both polarizations in the case of the $a$-plane sample, the modulus of the ratio of the $a$ and $b$ Raman tensor elements was estimated to be equal to 0.62. The angular dependence of the peak intensities of the $s$-plane sample grown on a non-nitridated substrate is clearly worse described compared to that of the sample grown on a nitridated one. Rapid thermal annealing has no effect on the angular dependence and consequently on the sample crystalline quality. The $\psi$-dependence of the Raman peak intensities for the $s$-plane grown on non-nitridated $\text{Al}_2\text{O}_3$ substrate was better modelled by assuming the presence of two hexagonal structural variants with different orientation in their $c$-axis ($\Delta \psi \sim 90^\circ$), as it is also identified by TEM and AFM. Thus, the intensity variation of the Raman peaks upon rotation of the sample is proved as a fast, non-destructive and very reliable method for the determination of the average content of the two structural variants. Furthermore, the width of the Raman peaks discloses the inferior crystalline quality of the $s$-plane sample grown on a non-nitridated substrate. Finally, from the relative to the strain-free values shift of the Raman peaks, we deduce that the samples experience tensile strain along the $[\bar{1}2\bar{1}0]$ and $[10\bar{1}0]$ directions and compressive strain along the [0001].

Acknowledgements

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Appendix

The unit vector matrices of the incident and scattered light with polarization along the OX axis can be expressed as:

\[
\hat{\epsilon}_i = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \text{ and } \hat{\epsilon}_s = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}
\]  

(A1)

whereas for polarization along the OY axis as:

\[
\hat{\epsilon}_i = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \text{ and } \hat{\epsilon}_s = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}
\]  

(A2)

The prime in \( \Re' \) of Eq. 2 denotes that the Raman tensor was subjected to a rotation transformation in order to be consistent with the growth orientation of the sample and the experimental geometry. The general displacement of a rigid body due to a rotation around a fixed point may be obtained by performing three rotations around two or three mutually perpendicular axes fixed to the body. We assume a right-handed coordinate system and we define a positive rotation around a given axis to be that which would cause a right-handed screw to advance along the positive direction of that axis. A rotation \( \psi \) \((0 \leq \psi \leq 2\pi)\) around the z axis of the body coordinate S(\(x,y,z)\) system will lead to a new S\(_1\)(\(x_1,y_1,z_1\) with \(z=z_1\)) system, a rotation \( \theta \) \((0 \leq \theta \leq \pi)\) around the \(y_1\) axis of the S\(_1\) system results to a new S\(_2\)(\(x_2,y_2,z_2\) with \(y_2=y_1\)) system and a rotation \( \phi \) \((0 \leq \phi \leq 2\pi)\) around the \(z_2\) axis of the S\(_2\) system to a new S\(_3\)(\(x_3,y_3,z_3\) with \(z_3=z_2\)) system.\(^57\) Equivalently, these rotations can be performed successively around the axes of the original system but with reverse order of the angles i.e. rotations of \( \phi \), \( \theta \) and \( \psi \) angles around the \(z\), \(y\) and \(z\) axes, respectively.\(^57\) The corresponding Euler matrix \( \Phi \) is:
\[ \Phi = \begin{pmatrix} 
\cos \theta \cos \phi \cos \psi - \sin \phi \sin \psi & \cos \theta \cos \psi \sin \phi + \cos \phi \sin \psi & -\cos \psi \sin \theta \\
-\cos \psi \sin \phi - \cos \theta \cos \phi \sin \psi & \cos \phi \cos \psi - \cos \theta \sin \phi \sin \psi & \sin \theta \sin \psi \\
\cos \phi \sin \theta & \sin \theta \sin \phi & \cos \theta 
\end{pmatrix} \] (A3)

Considering the Euler's matrix \( \Phi \) and its inverse \( \Phi^{-1} \), the crystal coordinates are transformed into the experimental ones and the Raman tensor \( \mathcal{R}' \) is given by:

\[ \mathcal{R}' = \Phi \mathcal{R} \Phi^{-1} \] (A4)

For the wurtzite structure, the Raman tensors \( \mathcal{R} \) of the vibrational modes are:

\[ \text{A}_1(\mathbf{z}): \begin{pmatrix} 0 & 0 & c \\
0 & 0 & 0 \\
0 & b & 0 \end{pmatrix}, \quad \text{E}_1(\mathbf{x}): \begin{pmatrix} 0 & 0 & 0 \\
0 & 0 & c \\
c & 0 & 0 \end{pmatrix}, \quad \text{E}_1(\mathbf{y}): \begin{pmatrix} 0 & 0 & c \\
0 & 0 & 0 \\
c & 0 & 0 \end{pmatrix} \]

and

\[ \text{E}_2^1 := \begin{pmatrix} d & 0 & 0 \\
-\frac{d}{2} & 0 & 0 \\
0 & 0 & 0 \end{pmatrix}, \quad \text{E}_2^2 := \begin{pmatrix} 0 & -d & 0 \\
-d & 0 & 0 \\
0 & 0 & 0 \end{pmatrix} \] (A5)

where \( a, b, c, d \) are the Raman tensor elements. \( \text{E}_1 \) and \( \text{A}_1 \) are polar modes, whereas the \( \text{E}_1 \) and \( \text{E}_2 \) modes are doubly degenerate. Symbols in parentheses \((x,y,z)\) designate the phonon polarization direction that corresponds to each mode described by the corresponding tensor. The Raman scattering intensity of the phonons of \( \text{E}_2 \) symmetry, is obtained by summing the two contributions from the two corresponding tensors. The same holds also for the \( x \) and \( y \) contributions of \( \text{E}_1 \). The equations that provide the dependence of the Raman peak intensities on the angles \( \phi, \theta \), and \( \psi \) for various polarization states of the impinging and scattering light are listed below. The Porto notation is adopted for the lab-fixed coordinate system.

The Raman peak intensities for \( \text{Z}(\mathbf{X})\mathbf{Z} \) geometry are:

\[ I_{\text{A}_1} \propto \left[ a \cos^2 \theta + \sin^2 \theta (b \cos^2 \psi + a \sin^2 \psi) \right]^2 \] (A6a)

\[ I_{\text{E}_{1x}} \propto 4c^2 \cos^2 \psi \sin^2 \theta (\cos \theta \cos \psi \cos \phi - \sin \phi \sin \psi)^2 \] (A6b)

\[ I_{\text{E}_{1y}} \propto 4c^2 \cos^2 \psi \sin^2 \theta (\cos \psi \cos \theta \sin \phi + \cos \phi \sin \psi)^2 \] (A6c)

\[ I_{\text{E}_2} \propto \frac{1}{16} d^2 (3 + \cos 20 - 2 \cos 2 \psi \sin^2 \theta)^2 \] (A6d)

whereas for the \( \text{Z}(\mathbf{Y})\mathbf{Z} \):
\[ I_{A_1} \propto \left[ a \cos^2 \theta + \sin^2 \theta (a \cos^2 \psi + b \sin^2 \psi) \right]^2 \]  
(A7a)

\[ I_{E_{1x}} \propto 4c^2 \sin^2 \theta \sin^2 \psi (\cos \psi \sin \phi + \cos \theta \cos \phi \sin \psi)^2 \]  
(A7b)

\[ I_{E_{1y}} \propto 4c^2 \sin^2 \theta \sin^2 \psi (\cos \psi \cos \phi - \cos \theta \sin \phi \sin \psi)^2 \]  
(A7c)

\[ I_{E_2} \propto \frac{1}{16} d^2 (3 + \cos 2\theta + 2 \cos 2\psi \sin^2 \theta)^2 \]  
(A7d)

And for the \( Z(XY)\bar{Z}, Z(YX)\bar{Z} \) geometries:

\[ I_{A_1} \propto (a - b)^2 \cos^2 \psi \sin^2 \psi \sin^4 \theta \]  
(A8a)

\[ I_{E_{1x}} \propto c^2 \sin^2 \theta (\cos 2\psi \sin \phi + \cos \theta \cos \phi \sin 2\psi)^2 \]  
(A8b)

\[ I_{E_{1y}} \propto c^2 \sin^2 \theta (\cos 2\psi \cos \phi - \cos \theta \sin \phi \sin 2\psi)^2 \]  
(A8c)

\[ I_{E_2} \propto \frac{1}{16} d^2 \left[ 16 \cos^2 \theta \cos^2 2\psi + \sin^2 2\psi (3 + \cos 2\theta)^2 \right] \]  
(A8d)
References

### Table I: Sample names and growth conditions of the InN epitaxial layers.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Orientation</th>
<th>Substrate nitridation</th>
<th>Buffer layer Type and growth temperature</th>
<th>Thickness (nm)</th>
<th>Temperature (°C)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN</td>
<td>$a$-plane (11\overline{2}0)</td>
<td>nitridation</td>
<td>GaN (450/715 °C)*</td>
<td>100</td>
<td>320</td>
<td>3000</td>
</tr>
<tr>
<td>SN</td>
<td>$s$-plane (10\overline{1}1)</td>
<td>nitridation</td>
<td>LT-InN (225 °C)</td>
<td>20</td>
<td>440</td>
<td>500</td>
</tr>
<tr>
<td>S</td>
<td>$s$-plane (10\overline{1}1)</td>
<td>-</td>
<td>LT-InN (225 °C)</td>
<td>20</td>
<td>440</td>
<td>500</td>
</tr>
<tr>
<td>S-RTA</td>
<td>$s$-plane (10\overline{1}1)</td>
<td>-</td>
<td>LT-InN (225 °C)</td>
<td>20</td>
<td>440</td>
<td>500</td>
</tr>
</tbody>
</table>

* two 50 nm-thick layers were sequentially grown at 450 and 715 °C.

Note: The sample S-RTA was a piece of sample S which was subjected to Rapid Thermal Annealing (RTA) at 650 °C for 1 sec under N₂ atmosphere
Table II: Raman peak intensities for specific sample orientations and experimental geometries. The labeling of a mode as longitudinal (LO) or transverse optical (TO) was done taking into account the propagation direction of the beam, the geometry of the experiment shown in Fig. 1 and the related discussion in Ref. 33. a, b, c and d are the Raman tensor elements. The frequencies $\omega$ of the corresponding LO and TO modes reported in the literature are also included.\textsuperscript{52,53,58,59}

<table>
<thead>
<tr>
<th>Mode symmetry</th>
<th>$\omega$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A_1$</td>
</tr>
<tr>
<td>$Z(XX)\bar{Z}$</td>
<td>$\psi=0^\circ$</td>
</tr>
<tr>
<td></td>
<td>$\psi=90^\circ$</td>
</tr>
<tr>
<td>$Z(XY)\bar{Z}$</td>
<td>$\psi=0^\circ$</td>
</tr>
<tr>
<td></td>
<td>$\psi=90^\circ$</td>
</tr>
<tr>
<td>$Z(YY)\bar{Z}$</td>
<td>$\psi=0^\circ$</td>
</tr>
<tr>
<td></td>
<td>$\psi=90^\circ$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mode symmetry</th>
<th>$\omega$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Z(XX)\bar{Z}$</td>
</tr>
<tr>
<td></td>
<td>$\psi=90^\circ$ $\neq$ 0 [LO &amp; TO]</td>
</tr>
<tr>
<td>$Z(XY)\bar{Z}$</td>
<td>$\psi=0^\circ$</td>
</tr>
<tr>
<td></td>
<td>$\psi=90^\circ$</td>
</tr>
<tr>
<td>$Z(YY)\bar{Z}$</td>
<td>$\psi=0^\circ$</td>
</tr>
<tr>
<td></td>
<td>$\psi=90^\circ$</td>
</tr>
</tbody>
</table>
**Table III:** Frequency shifts, $\Delta \omega$ (in cm$^{-1}$), of the $E_{1}$(TO) and $E_{2}^{b}$ Raman peaks (average values for the $\hat{e}_{i} \parallel OX$ and $\hat{e}_{i} \parallel OY$ polarizations) relative to the corresponding values for strain-free samples, 477.9 and 491.1 cm$^{-1}$, respectively.$^{52,53}$ The obtained strain values are also listed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta \omega_{E_{1}(TO)}$</th>
<th>$\Delta \omega_{E_{2}^{b}}$</th>
<th>$\varepsilon_{xx} = \varepsilon_{yy}$</th>
<th>$\varepsilon_{zz}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SN</td>
<td>-2.4±0.2</td>
<td>1.3±0.1</td>
<td>0.007</td>
<td>-0.012</td>
</tr>
<tr>
<td>S</td>
<td>-3.3±0.1</td>
<td>0.0±0.1</td>
<td>0.007</td>
<td>-0.010</td>
</tr>
<tr>
<td>S-RTA</td>
<td>-3.5±0.2</td>
<td>-0.1±0.2</td>
<td>0.007</td>
<td>-0.010</td>
</tr>
<tr>
<td>AN</td>
<td>-3.2±0.2</td>
<td>-1.4±0.1</td>
<td>0.004</td>
<td>-0.004</td>
</tr>
</tbody>
</table>
**Figure Captions**

**Figure 1:** (a) Geometry of the Raman experiment. $OXYZ$ and $Oxyz$ are the lab- and sample-fixed coordinate systems. The sample orientation and rotation is described by the Euler angles $\psi$, $\theta$, $\phi$. (b,c) Definition of the $a$- and $s$-planes with respect to the hexagonal unit cell. (d,e) Hexagonal unit cell relative to the sample that was positioned horizontally. (f) Raman-active vibrational modes in wurtzite structure and wave vectors of the involved phonon ($\vec{q}$) and incident ($\vec{k}_i$) and scattered ($\vec{k}_s$) photons in the backscattering configuration for the Stokes Raman process.

**Figure 2:** Typical Raman spectra of the AN sample ($\alpha$-plane) recorded for incident light polarization vector (a) $\hat{e}_i \parallel OX$ and (b) $\hat{e}_i \parallel OY$, as defined in Fig. 1. Typical representative fittings using Lorentzian lineshapes are shown in thick solid lines. The spectra are vertically shifted for clarity.

**Figure 3:** Typical Raman spectra of the SN sample ($s$-plane) recorded with the laser polarization vector (a) $\hat{e}_i \parallel OX$ and (b) $\hat{e}_i \parallel OY$, as defined in Fig. 1. Typical representative fittings using Lorentzian lineshapes are also shown in thick solid lines. The spectra are vertically shifted for clarity.

**Figure 4:** Dependence of the normalized Raman peak intensities of the $A_1$(TO), $E_1$(TO) and $E_2^h$ modes on the angle $\psi$ for the sample AN ($\alpha$-plane) with the laser light polarization vector (a) $\hat{e}_i \parallel OX$ and (b) $\hat{e}_i \parallel OY$. Filled circles correspond to experimental values normalized to the maximum intensity of each peak. Solid lines correspond to best fits of the theoretical expressions to the experimental data.

**Figure 5:** Dependence of the normalized Raman peak intensities for $Q$(TO), $E_1$(TO) and $E_2^h$ on angle $\psi$ for the ($s$-plane) samples S and SN with exciting polarization vector (a) $\hat{e}_i \parallel OX$ and (b) $\hat{e}_i \parallel OY$. Filled circles (sample SN), filled squares (sample S) and empty squares (sample S-RTA) correspond to the experimental values normalized to the maximum intensity of each peak. Solid and dashed lines denote the $\psi$-dependence predicted by the theory, considering one and two structural modifications, respectively.
**Figure 6:** Cross sectional bright field TEM images along the \([20\bar{2}\bar{1}]\) sapphire zone axis of (a) sample S, and (b) sample SN. In (a) arrows indicate crystallites of the two InN orientation variants. Crystallites belonging to the variant that is viewed along \([\bar{1}\bar{1}\bar{2}0]\) \(\text{InN}\) are distinguished by the observation of edge-on basal stacking faults. Only threading dislocations are well discernible in the variant viewed along \([\bar{2}113]\) \(\text{InN}\). Sample SN exhibits fewer crystallites viewed along the \([\bar{1}\bar{2}10]\) \(\text{InN}\) zone axis that are confined close to the interface as indicated by arrows.

**Figure 7:** Phase-contrast AFM image of the sample S-RTA with the arrows indicating crystallites belonging to the two structural variants.
FIGURE 2
FIGURE 3
FIGURE 4