Holmi, Joonas; Bairamov, Bakhshy H.; Suihkonen, Sami; Lipsanen, Harri

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Identifying threading dislocation types in ammonothermally grown bulk α-GaN by confocal Raman 3-D imaging of volumetric stress distribution

J.T. Holmi⁎, B.H. Bairamovb, S. Suihkonena, H. Lipsanena
a Department of Electronics and Nanoengineering, Aalto University, P.O. Box 13500, FI-00076 Aalto, Espoo, Finland
b Ioffe Institute, St. Petersburg 194021, Russia

A B S T R A C T

This study demonstrates all-optical Raman scattering study of dislocations in ammonothermally grown α-GaN crystal and identifies an edge $\overline{a}$-type threading dislocation (TD) using a confocal Raman 3-D imaging technique. These findings make possible the characterization of volumetric stress field and low TD density distributions over a large area on bulk α-GaN single crystal. The dislocation type effects on Raman shift are also discussed in detail (in order to identify the edge $\overline{a}$-type and mixed $\overline{a} + \overline{c}$-type TDs, and theorize the invisibility of the screw $\overline{c}$-type TDs). Authors are not aware of any previous reports using the confocal Raman 3-D imaging to identify the edge $\overline{a}$-type and mixed $\overline{a} + \overline{c}$-type TDs.

1. Introduction

The wide direct bandgap, piezo-electric, wurtzite-structure α-gallium-nitride (α-GaN) is a valuable material for the development of optical and optoelectronic applications, including highly efficient blue light-emitting diodes [1,2] (with tunable colours by quantum dots [3]) and laser diodes [4], high power devices for communications, radar and power amplifiers, and detectors for blue and ultraviolet light [5,6]. It also exhibits a low thermo-optic coefficient, high chemical stability and optical damage threshold, and suits for high operating temperatures. Currently, a majority of α-GaN crystals are grown by hydride vapor phase epitaxy (HVPE), enabling up to 4-inch wafers with mid-10$^{15}$ cm$^{-3}$ TD densities and controllable electron concentration down to 10$^{14}$ cm$^{-3}$ [7]. Unfortunately, the HVPE-grown crystals suffer from limited thickness in the c-direction due to wafer bowing and crack formation induced by parasitic growth and internal stresses [8,9]. At present, the ammonothermal synthesis is one of the most promising commercially available methods, which enables industrial-scale, low-cost growth of bulk single crystals of α-GaN at high crystalline quality. The latest advances allow a very low reproducible 10$^4$ cm$^{-2}$ TD densities [10,11], large arbitrarily-oriented substrates [12], and growth rates in the c-direction of about 350 μm/day [13], although slow compared to HVPE. Wafers sliced from the boule have excellent radius of curvature of about 600 m [14] and have been successfully used in homoepitaxy for III-N devices (see Ref. [15] for a recent review).

Despite the apparent success in the crystalline quality of the as-grown ammonothermal α-GaN crystals, there still remains many further questions about the mechanism of their crystallization and the nature of the intrinsic properties. For instance, the use of their key properties for very promising device applications are hindered by the presence of a high background impurity concentration (in the range of 10$^{15}$–10$^{21}$ cm$^{-3}$ [15]) and other defects, such as edge $\overline{a}$-type, screw $\overline{c}$-type, and mixed $\overline{a} + \overline{c}$-type TDs. These dislocations in particular cause undesired local residual stresses in the grown lattice and they are still not well understood nor easily identifiable in the α-GaN samples. Currently, there is no standardized method to characterize the dislocation density and types in α-GaN, even though few good options already exist such as defect selective etching (DSE) and synchrotron radiation X-ray topography (SR-XRT) [16]. However, these cannot conveniently and non-destructively be utilized to follow the dislocation propagation and interaction inside the grown crystal, although recently a successful multi-tool correlating study was done to construct three-dimensional (3-D) images of the dislocations [17]. For this reason, the viability of confocal Raman spectroscopy for identifying dislocations in α-GaN is explored in this work. Raman spectroscopy is a non-destructive study of the unique molecular vibrational characteristics by the inelastic light scattering of...
light. Although residual stresses in the as-grown α-GaN single crystals are already well studied by Raman spectroscopy via the peak shift of the main α-GaN Raman modes [18–22] (for at least two decades [23] and also in 3-D [20,21]), only a recent Raman study by N. Kokubo et al. (2018) [24] has reported to have utilized Raman 2-D maps to intentionally estimate the TD densities and identify the edge σ-component directions in the material, but none has used the full potential of the confocal Raman microscopy, the diffraction-limited 3-D imaging capability.

Hence, the authors demonstrate the capabilities of an all-optical Raman study of ammonothermally grown α-GaN crystal by identifying one edge σ-type TD using the confocal Raman 3-D imaging technique, revealing the stress distribution induced by the dislocation and the background impurities through the Raman shift of $E_2^R$. Surprisingly, the confocal Raman 3-D imaging technique has only recently gained some popularity [20,25–27], although it has been around for almost three decades [28]. This is understandable after considering the main challenges in using the technique, which lie in the handling of the various potential error sources that can interfere with the volumetric scan process in real-time [27,29,30], and in the post-processing and dimensionality reduction of the hyperspectral (4-D) dataset (1-D spectrum for each spatial 3-D pixel) [25]. Otherwise Raman is particularly useful because of its ability to simultaneously and non-destructively collect many material structural parameters, including doping and stress, into each of its spectrum. Main objectives of this study are then to (1) enable a successful confocal Raman 3-D imaging experience, (2) discuss the dislocation type effects on Raman shift in detail (in order to identify the edge σ-type and mixed σ + τ-type TDs, and theorize the invisibility of the screw τ-type TD), (3) estimate the TD density (for edge σ-type and mixed σ + τ-type TDs) over a large area by Raman scattering, and (4) demonstrate the edge σ-type TD propagation into the material by the 3-D imaging technique. In other words, this study aims to present Raman scattering as a suitable supporting tool for the dislocation characterization of any low TD density α-GaN, in hopes to advance the understanding of the α-GaN dislocation interaction and propagation mechanisms. The novelties in this work are the first Raman spectroscopic attempt to identify the edge σ-type TD from its volumetric biaxial stress distribution below the Ga-polar surface while intentionally estimating the TD density with σ-content from a much wider 2-D Raman shift map.

2. Experimental

2.1. Sample preparation

The studied $10 \times 10 \times 0.4$ mm$^3$ piece of c-oriented bulk α-GaN was grown by the ammonothermal method, using basic chemistry [31]. The Ga-side c-surface was polished to epi-ready quality. It has a high carrier concentration as indicated later by the Raman measurements in Fig. 1. Oxygen is believed to be the dominant dopant as indicated by Sintonen et al. (2016) [32,33] and Suhihkonen et al. (2017) [15].

2.2. Characterization: Confocal Raman spectroscopy

Commercial confocal Raman microscope, WITec alpha300 RA was used for high spatial resolution Raman scattering imaging. It was equipped with an ultra-high throughput spectrometer with 1800 g/mm grating and a back-illuminated electron-multiplied CCD camera detector, Andor Newton DU970N-BV-353, thermoelectrically cooled to $-60$ °C. High confocality was achieved by high magnification and numerical aperture $\times 100/0.95$ dry objective lens and 25 μm core diameter multi-mode detection fiber. The sample movement was controlled in a few nm precision with an XY(Z) piezo stage. For better stability, the Raman spectrocope is situated in the temperature, relative humidity and pressure differential controlled cleanroom at ambient conditions of 21.11(7) °C, 44.9(5) %RH and 30(3) dPa, respectively. Laser excitation wavelength of 488 nm was utilized in this work. For the most part, 30 mW power was used for the best signal, but 1.25 mW was used to determine the bulk hydrostatic stress state without the heating effect. In case of high power, laser induced heating and stress effect on the Raman peak shift [34] was found to be +0.07(2) cm$^{-1}$ or less. Raman measurements in this study utilized point, area and volume scans.

2.3. Post-processing: Spectral nonlinearity calibration

One aim of this work was to determine the average hydrostatic stress in the α-GaN sample using precise knowledge of the Raman peak position of $E_2^R$. The main obstacle is the requirement for the spectro-meter calibration, which determines the spectral axis and is easily unintentionally affected by the current state of the environment. In case of the pixel array detection, the spectral axis can also become significantly nonlinear for various reasons, shifting both the laser wavelength and the peak of interest in nonlinear way. Fortunately, the spectral axis can be calibrated and linearized after measuring spectral atomic lines of a calibration lamp with well-known reference standards, available at Atomic Spectra Database by National Institute of Standards and Technology (NIST ASD) [35]. If this is done right before or after the actual measurements, then the calibration remains valid and absolute Raman spectroscopic features can be restored.

The spectral axis calibration of three widely-spaced 10-min-long point scans was done as a post-processing step in order to extract the needed mean absolute hydrostatic stress in the bulk volume. It was carefully checked from the CCD nonlinearity measured using 34 spectral atomic lines of a neon lamp. The 1σ-noise was ~0.1 cm$^{-1}$ after removal of the dark current background and the cosmic ray spikes. The Raman peak position, $\text{Pos}(E_2^R)$ was found to be upshifted by $+0.96(28)$ cm$^{-1}$ instrumental shift, predicted by a photon noise weighted third order polynomial spectral correction fit. The remaining 1σ-uncertainty of instrumental shift (in parenthesis) leads to a significant uncertainty in the reported absolute stress values. It is caused by the uncertainty in Voigt-fitting of the sparse and low intensity neon atomic lines near the peaks of interest.
2.4. Post-processing: Raman map scanline error correction

The 2-D biaxial stress distribution of the α-GaN Ga-polar surface was estimated from the peak position of \( E_2^\alpha \) Raman mode, \( \text{Pos}(E_2^\alpha) \), obtained through the single Lorentzian lineshape fitting. All of the reported 2-D maps have been corrected from scanline errors, which arise due to piezo-stage trace-retrace movement, microscope drifts and arbitrary fluctuations in the cleanroom environment, such as acoustic and mechanical noise. Median of line differences (an inverse log-transformed version of median of line ratios, aided by automatically generated flatness mask) [36] was found as a robust and useful algorithm to correct all such scanline errors. Nevertheless, it was impossible to fully correct those more rarely occurring partial scanline errors, which are seen in Fig. 2b background. Successful scanline and z-plane corrections were especially essential for the 3-D isosurface rendering of the edge \( \alpha \)-type TD shown in Fig. 4.

2.5. Post-processing: Depth axis rescaling

Diffraction-limited 3-D measurements in confocal Raman microscope require a tightly focused laser beam through an objective lens onto the sample, which is moved in atomic precision under the beam with a piezo stage in three dimensions. Unfortunately, an abrupt change in the refractive index at the air/α-GaN-interface causes the laser spot to focus in different depth than predicted by the piezo z-sensor of the microscope. Effects of numerical aperture and refractive index change were accounted for by scaling factor of 3.7 [37] to estimate the real c-axis below the α-GaN Ga-polar surface, which was found at the first order derivative maximum of the intensity depth profile [38].

3. Results and discussion

3.1. Average Raman spectrum: The average free carrier concentration and hydrostatic stress in the bulk

The Raman measurements were performed in the \( z(xx+yy)\xi \) backscattering geometry, where z-axis corresponds to the Ga-polar direction, \( c^-\)-axis or [0001], x-axis to the m-axis or [\( 1\overline{1}00 \)], and y-axis to the a-axis or [1120]. The summation, \( xx+xy \) indicates the unpolarized light detection, whereas the first \( x \) means the incident light polarization along the m-axis. The Raman spectrum of the studied bulk α-GaN sample averaged over \( 50 \times 50 \) \( \mu \text{m}^2 \) area is depicted in Fig. 1. The vibrational excitations cause the Raman spectrum to exhibit the spectral response properties characteristic of the heavily doped n-type α-GaN. High free carrier concentration of \( n \approx 2.46 \times 10^{19} \) \( \text{cm}^{-3} \) was estimated from the visible and highly up-shifted lower longitudinal optical (LO) phonon-plasmon coupled (LPP') mode centered at 499.14(29) \( \text{cm}^{-1} \) using the previously reported correlation with the free carrier concentration by Kuball (2001) [39]. In the case of p-type doping, both LPP' and LPP" modes in Raman shift are considerably less sensitive to the hole concentration and LPP" should be visible near \( 736 \text{ cm}^{-1} \) for the realistic concentration values [40]. Impurity atom induced Raman mode, \( P_2 \) is believed to be at \( \approx 420 \text{ cm}^{-1} \) [41]. Theoretically forbidden transverse optical (TO) mode, \( E_2(\text{TO}) \) is also seen here because of the used high numerical aperture objective lens, since the incident laser beam is not strictly parallel to the c-axis. This could be mitigated by the use of low numerical aperture objective lens, what may also aid the lineshape fitting of \( E_2^\alpha \) in the typically noisy 3-D imaging situations.

Currently, there is no reliable and verified data for stress-free α-GaN, as all reports are on material either heteroepitaxially grown on lattice-mismatched substrates, such as Si or sapphire, or contain high concentration of defects and impurities, which affect the stress state of the crystal. In this work we used the linear dependence between the Raman peak position, \( \text{Pos}(E_2^\alpha) \) and the c-plane biaxial stress, \( \sigma_\alpha \), presented by Lu et al. (2011) [19] (shown in inset of Fig. 1), from which the hydrostatic stress, \( \sigma_0 \), contribution to the shift has already been subtracted away. The relation is written as

\[
\text{Pos}(E_2^\alpha) = 566.65 - 3.43 \cdot \sigma_\alpha - 4.205 \cdot \sigma_\alpha^H - \frac{\omega_0 - \omega_0^H - \sigma_0}{\omega_0} \sigma_\alpha^H - \omega_0 + \overline{\beta} \cdot (\omega_\alpha + \overline{\sigma} \cdot \alpha + \overline{\sigma} \cdot x) + \frac{\overline{\beta}}{2} \cdot \sigma_0^H,
\]

where \( \overline{\sigma} = -(2 \overline{\alpha} + \overline{\beta}) \) and \( \overline{K} = -2 \overline{\alpha} \). This assumes unstrained \( \text{Pos}(E_2^\alpha) \) frequency of \( \omega_0 = 566.65 \text{ cm}^{-1} \) through interpolation. Although the relation was obtained using 514 nm laser excitation wavelength, the phonon deformation potentials for α-GaN are believed to be fairly wavelength insensitive.

The average \( \text{Pos}(E_2^\alpha) \) in the bulk was obtained by averaging three widely-spaced 10-min-long low power point scan measurements, 600
data point time series per point. After Voigt-fitting and meticulous corrections (see details in Section 2.3) using neon atomic line references from NIST ASD [35], it was obtained that $\text{Pos}(E_{2}^{fi})$ in the Ga-side bulk $\alpha$-GaN is 567.40(28) cm$^{-1}$ with $\sigma$-confidence interval in the parenthesis. This corresponds to absolute hydrostatic stress of $-179(67)$ MPa, when assuming zero biaxial stress in the uniform areas of the bulk. Authors believe that ammunothermally grown low TD density $\alpha$-GaN is dominated by the hydrostatic stress due to the high impurity concentration, which are point defects and generate hydrostatic stress in the lattice [42-47]. For instance, high concentrations of oxygen (silicon) impurities are known to expand (shrink) the lattice almost uniformly [47,45], causing tensile (compressive) hydrostatic stresses in the bulk material. Such impurities are thought to be introduced during the ammonothermal growth conditions [15]. However, the implied compressive hydrostatic stress of $-179$ MPa is in contradiction with the expected oxygen dominance [15,32,33], which causes tensile stresses [47]. One could reason that the discrepancy is caused by sufficient amount of other less dominant impurity atoms such as Si, which modulate the lattice constants in the opposite way three times stronger than oxygen [47], but this is highly unlikely due to many contrary examples of defect incorporation distributions such as by Sintonen et al. (2016) [33]. Second option is the fact that our Raman has significant CCD nonlinearity calibration $\sigma$-uncertainty, but this is still not enough to down-shift $\text{Pos}(E_{2}^{fi})$ into the tensile stressed region required by the expected oxygen dominance. The most probable explanation is an unintentional instrumental shift in the interpolated stress free value, $\omega_0$ due to lack of proper spectral nonlinearity calibration, which was not mentioned by Lu et al. [18,19]. This discrepancy will be a subject to be investigated in the future work.

3.2. 2-D Raman imaging: The spectral uniformity and the density of TDs with $\vec{a}$-content (in Burgers vector)

In order to see the biaxial stress field distribution on the Ga-polar surface, optically video captured in Fig. 2a, a $50 \times 50 \mu m^2$ wide area was confocally Raman 2-D imaged, what is illustrated in Fig. 2b. At least 20 defects are seen in this scan image Fig. 2b, excluding those which either do not generate detectable Raman peak shift, such as pure screw $\vec{c}$-type TD (discussed later in this section), or are situated too close to each other to be detected separately [16]. None of them forms large enough cluster to be seen in the optical image, Fig. 2a. This count is utilized to give a lower bound estimate for the density of TDs with $\vec{a}$-content in Burgers vector of an ideally uniform sample: $> 8 \times 10^{5}$ cm$^{-2}$, which is rather low [15], but Sintonen et al. (2014) has demonstrated even lower TD density for similar sample [16]. One of the dislocations, marked with blue square, was chosen to be investigated further through the 3-D imaging technique.

The Raman peak shift of $E_{2}^{fi}$ is in general sensitive to any linear combination of uniaxial stresses ($\sigma_{xy}$, $\sigma_{yy}$, and $\sigma_{zz}$) and experiences peak splitting (or thus broadening) in presence of shear stresses ($\sigma_{xx}$, $\sigma_{yx}$ and $\sigma_{yz}$, and their symmetric counterparts) [48-50]. However, the fact that shear stresses do not produce any measurable shift in Pos($E_{2}^{fi}$) (except splitting or broadening), it was possible to completely neglect them in this analysis of Pos($E_{2}^{fi}$). This simplification is further supported by the in-depth analysis (later in this section) of the dislocation types and the deformation they cause. It was also assumed that the intrinsic deformation in the $\alpha$-GaN lattice is a superposition of biaxial ($\sigma_{xz} = \sigma_{yz} = \sigma_0$ with $\sigma_{xx} = \sigma_{yy} = 0$) and hydrostatic ($\sigma_{xy}^H = \sigma_{yx}^H = \sigma_{yz}^H = \sigma_0$) components of stress, and cannot have lone uniaxial $\sigma_{xx}^U$ or $\sigma_{xx}^U$ components of stress without external forces. This is the route to the compact relation for Pos($E_{2}^{fi}$) by Lu et al. [19], expressed earlier in inset of Fig. 1. Authors believe that the deformation in the ammonothermally grown $\alpha$-GaN is mainly caused by a constant hydrostatic component of stress, $\sigma_0$ due to the uniform high impurity concentration within the scan region. This simplification allows easy subtraction of the hydrostatic stress contribution to the Raman shift and direct estimation of the absolute biaxial component of strain, $\omega_0$ in the non-uniform Pos($E_{2}^{fi}$) in Fig. 2b. For these reasons, both hydrostatic and biaxial stresses, $\sigma_0$ and $\omega_0$ contribute to the Raman shift seen in Fig. 2b, but the hydrostatic stress alone causes the background level.

There are three main types of dislocations in c-plane $\alpha$-GaN: edge $\vec{a}$-type, screw $\vec{c}$-type and mixed $\vec{a} + \vec{c}$-type TDs (a mixture of first two), where the vectors ($\vec{a}$ and $\vec{c}$) represent the direction of the lattice distortion, also hereafter denoted as the Burgers vector components, either in one of the a- or c-axis directions. The edge $\vec{a}$-type TD causes biaxial component of stress, $\omega_0$ and uniaxial stress, $\sigma_{yy}^H$ (51-53) along with non-zero shear stress in c-plane, $\sigma_{xy}$, neglected in this study. Importantly, low Poisson’s ratio, $\nu = 0.1830(3)$ for $\alpha$-GaN [54] ensures that $\omega_0$ is significantly larger than $\sigma_{yy}^H$ [51,52]. The screw $\vec{c}$-type TDs behave differently and generate only two kinds of shear stress, $\sigma_{xy}$ and $\sigma_{yx}$, but its shear stress in c-plane, $\sigma_{xy}$ is still zero [51,52]. It is important to recognize that $\sigma_{xy} = \sigma_{yx} = \omega_0 = 0$ (and $\sigma_{yy}$ = 0) for the screw character, all of which could have been detected when non-zero by Raman peak shift (and split) [48-50]. This implies that the screw $\vec{c}$-type TDs are not detectable by means of Raman peak shift, at least theoretically, in case of the $E_{2}^{fi}$ phonon experimentally verified by a recent Raman study by N. Kokubo et al. (2018) [24]. To authors’ best knowledge, phonon deformation potential, $\omega_0$ for out-of-plane shear stresses has not yet been reported for $\alpha$-GaN, even though it was found zero for $\pi$-CdS [48]. This appears to convey that the screw character may not generate detectable Raman peak broadening at all, which should be put to test in the future. As a consequence, it may then be challenging to distinguish the edge $\vec{a}$-type TD from the mixed $\vec{a} + \vec{c}$-type TDs, which have both edge and screw character (approximately independent from each other [51]). Nevertheless, the treatment in Fig. 2b is particularly useful, because deviation from the average Pos($E_{2}^{fi}$) is mainly caused by $\omega_0$, which dominates around the edge $\vec{a}$-type and mixed $\vec{a} + \vec{c}$-type TDs [51-53,55]. But atomic-scale studies have shown that the mixed $\vec{a} + \vec{c}$-type TD (with larger Burgers vector) are fundamentally different from the edge $\vec{a}$-type TD [53,55-58]. For instance, it is calculated to have a stronger and more far-reaching stress field [59], what could be utilized to distinguish it from the pure edge $\vec{a}$-type TD. As this is beyond the scope of this work, more experimental work is needed to test these theoretical implications.

3.3. 3-D Raman imaging: Z-stack representation of the biaxial stress field distribution around a dislocation

Confocal Raman microscopy at its best can be used to collect 1-D spectra for each spatial 3-D pixel, generating a vast hyperspectral dataset. Time-consuming post-processing, such as Lorentzian lineshape fitting like in this work, is often performed to reduce this 4-D dataset into several more useful 3-D datasets for each property of the peaks of interest. This is the birth of the confocal Raman 3-D imaging technique, which has successfully been utilized in few recent studies [20,25-27]. Optically transparent materials such as $\alpha$-GaN (and its defects) are particularly suitable for such diffraction-limited volumetric analysis. The main novelty of this work is the first attempt to volumetrically identify the edge $\vec{a}$-type TD from its biaxial stress distribution.

Volumetric z-stack of XY-images, depicted in Fig. 3, was collected within $3 \times 3 \mu m^2$ area, previously marked by the blue square in Fig. 2a and b. Total number of 13500 Raman spectra, 250 ms integration time per spectra was gathered within total acquisition time of 1 h 15 min. For reasons described in previous Section 3.2, this area contains one either edge $\vec{a}$-type or mixed $\vec{a} + \vec{c}$-type TD core and its biaxial stress field distribution encoded as Pos($E_{2}^{fi}$) shifts. This long range visualization of the biaxial stress distribution displays well the compressive (bright) and tensile (dark) stressed regions characteristic to the dislocations with edge character and appears to be similar to that of the recent atomic-scale study by Xiong et al. (2018) [55]. However, it is noted here that the true shape is smoothened out by oversampling (1 px = 100 nm in the lateral direction), because the Pos($E_{2}^{fi}$) data is strongly convoluted
3-D rendered biaxial stress isosurfaces:
- compressive
  - stress level: 568.385 cm\(^{-1}\)
  - stress magnitude: 9.7090 MPa
- tensile
  - stress level: 568.4375 cm\(^{-1}\)
  - stress magnitude: -0.3260 MPa

Six stress field gradient orientations in c-plane:
- air/\(\alpha\)-GaN-interface
- \(\alpha\)/Ga-side interface

Six Burgers vectors in \(\langle 11\overline{2}0\rangle\) direction

3.4. Volume rendering of the compressive and tensile stress isosurfaces around the dislocation

Previously represented volumetric z-stack of Pos\((E^2)\) maps in Fig. 3 was post-processed further in order to merge the stack together into the 3-D dataset. This was already shown to be a particularly challenging task due to various potential error sources that can interfere with the volumetric scan process, what is perhaps the main reason that confocal Raman 3-D imaging technique is still not widely utilized despite being available for nearly three decades \[28\]. Here the piezo-stage error induced lateral drift was also compensated by performing the depth scan in the forward–backward manner, where half of the slices were forward-scanned and other half backward-scanned. This allowed following the dislocation core position via interpolation and correcting any deviation from linear change in its location. Allowing linear movement of the dislocation core is based on the fact that, for instance, the mixed \(\vec{a} + \vec{c}\)-type TD have been reported to have non-zero inclination angle \[58,60,61\]. In addition, the \(z\)-axis was rescaled by 3.7 \[37\] below the Ga-side interface (shown as a plane) to estimate the real c-axis, which was distorted due to abrupt change in the refractive index. Illustration of the six possible gradients between the minimum and maximum of the stress field (along with the Burgers vector \(\vec{a}\)-components) were adapted from study by Sintonen et al. \(2014\) \[16\], supported by a recent Raman study \[24\] and atomic-scale studies, such as ab initio calculation by Xiong et al. \(2018\) \[55\]. This dislocation then has the Burgers vector \(\vec{a}\)-content in direction of \(\langle 11\overline{2}0\rangle\) (down). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Due to a long total scan duration, Pos\((E^2)\) scans were anomalously shifted in Fig. 3 by various instrumental and environmental causes, described in more detail in Section 2.4. This anomalous peak shift occurred both in scanline and depth cross-sections. Fortunately, the scanline errors were readily corrected by median of line distribution. Moreover, Raman peak shift \(z\)-drift was corrected by median z-plane \(σ_\text{pp}^\text{E}^2\). This was already shown to be a particularly challenging task due to various potential error sources that can interfere with the volumetric scan process, what is perhaps the main reason that confocal Raman 3-D imaging technique is still not widely utilized despite being available for nearly three decades \[28\]. Here the piezo-stage error induced lateral drift was also compensated by performing the depth scan in the forward–backward manner, where half of the slices were forward-scanned and other half backward-scanned. This allowed following the dislocation core position via interpolation and correcting any deviation from linear change in its location. Allowing linear movement of the dislocation core is based on the fact that, for instance, the mixed \(\vec{a} + \vec{c}\)-type TD have been reported to have non-zero inclination angle \[58,60,61\]. In addition, the \(z\)-axis was rescaled by 3.7 \[37\] below the Ga-side interface (shown as a plane) to estimate the real c-axis, which was distorted due to abrupt change in the refractive index. Illustration of the six possible gradients between the minimum and maximum of the stress field (along with the Burgers vector \(\vec{a}\)-components) were adapted from study by Sintonen et al. \(2014\) \[16\], supported by a recent Raman study \[24\] and atomic-scale studies, such as ab initio calculation by Xiong et al. \(2018\) \[55\]. This dislocation then has the Burgers vector \(\vec{a}\)-content in direction of \(\langle 11\overline{2}0\rangle\) (down). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
D isosurfaces, which represent constant value contours, in this case tensile and compressive biaxial stresses. They were chosen arbitrarily to give a good representation of the two stress contours near dislocation core without being obscured by background noise level. The 3-D illustration in Fig. 4 immediately implies that the dislocation is inclining with an angle of 5° in direction of a-axis. Determination of the dislocation inclination angle is important and can potentially be used to distinguish the mixed $\vec{\alpha} + \vec{\sigma}$-type TD from the edge $\vec{\alpha}$-type TD, because inclination angles of 12.2° (15.6° in theory) and 0° towards the Burgers vector edge $\alpha$-component have been reported for the mixed $\vec{\alpha} + \vec{\sigma}$-type and edge $\vec{\alpha}$-type TDs, respectively [60], although this can be perturbed by various imperfections during the growth process [58,60,61]. It is noteworthy that the mixed $\vec{\alpha} + \vec{\sigma}$-type TDs have an energy minimum in a fixed inclination angle towards the Burgers vector edge $\vec{\alpha}$-component, whereas the edge $\vec{\alpha}$-type TDs are energy-minimized to a zero angle [60]. Authors believe that ammonothermally grown a-GaN has sufficiently high crystalline quality in order to satisfy this condition. While there can be a minor c-plane miscut, sample bow and surface polish imperfections, they are unlikely to be in such a scale. Considering the smallness of 5° angle, authors believe it to be an instrumental artefact due to a slightly off-center laser focusing. In other words, this particular dislocation would then appear to be the edge $\vec{\alpha}$-type TD based on its nearly zero inclination angle.

Thinning (broadening) of the tensile (compressive) isosurface, seen in Fig. 4 when progressing deeper, is not a real feature but rather an unintentional artefact from the imperfect correction of the anomalous z-drift in Pos(E\text{\,f})\text{\,(2)}\text{\,(4)}. One limiting factor is believed to be the measurement 1z-uncertainty of 0.01–0.02 cm$^{-1}$ (3.4–6.9 MPa). This z-drift issue could be mitigated by modified CRS detection using real-time neon calibration lamp via bifurcated detection fiber technique [29], which is planned to be utilized in the future. Simultaneously, the scanline errors could be removed and, at best, spectral axis nonlinearity calibrated in real-time. Another misleading visual feature in Fig. 4 is that the isosurfaces appear above the Ga-side interface in air, but this is understood as the laser point spread function convolution effect, which means that the Raman scattering volume is still partially inside the sample. These should be taken in careful consideration when interpreting the 3-D Raman data.

Study by Sintonen et al. (2014) [16] reports that the stress field dipoles like in Figs. 3 and 4 can only be oriented in six different ways, experimentally verified by a recent Raman study by N. Kokubo et al. (2018) [24]. Ab initio calculations [53,55,57,62] and scanning transmission electron microscope studies [58,63] confirm the sixfold symmetry for the stress field dipole orientation in the case of the edge $\vec{\alpha}$-type and mixed $\vec{\alpha} + \vec{\sigma}$-type TDs. These stress fields are bound to the same symmetries as their host dislocations, in which the stresses are generated by the displaced atoms (and their bonds) in the dislocation core, illustrated best in [55]. This 6-fold rotation symmetry in c-plane for the dislocation core orientation (and the corresponding stress field dipole) is a direct consequence of the 3-fold rotation symmetry in c-plane for the a-GaN hexagonal lattice and the 180° changes in the c-plane symmetry by the consecutive c-plane atomic steps. For the same reason, the edge $\vec{\alpha}$-type TD always has its Burgers vector along one of the six $\vec{\alpha}$-directions. This information was used to determine that the dislocation shown in Figs. 3 and 4 has the edge $\vec{\alpha}$-component of Burgers vector along [1120] (pointing down in Fig. 3). However, this study is not sufficient to determine if this edge $\vec{\alpha}$-type TD has the most common and energetically favourable 5/7-atom ring core [57,58,63], due to the fundamental diffraction limitation of confocal Raman microscopy.

4. Conclusions

This study focused on the 1-D, 2-D and 3-D stress distribution analysis of the Raman peak shift, Pos(E\text{\,f})\text{\,(2)}\text{\,(4)} for the Ga-polar c-plane of the ammonothermally grown a-GaN with TDs. Three widely-spaced 10-min-long point scan measurements were analyzed after correcting them for the spectral axis nonlinearities using a neon calibration lamp. The average Pos(E\text{\,f})\text{\,(2)}\text{\,(4)} was found to be 567.40(28) cm$^{-1}$, where the value in parenthesis represents the 1σ-confidence interval due to the calibration uncertainty. This shift from the interpolated stress free value of 566.65 cm$^{-1}$ [19] implied an absolute compressive hydrostatic stress of $-179(67)$ MPa, supposedly caused by the impurity atoms, but was found to be in conflict with the previously reported evidence of oxygen dominance [15,32,33], which instead produces tensile stresses [47]. For this reason, the used stress free value is put in doubt by the authors in Section 3.1 and is expected to be unintentionally biased due to lack of spectral nonlinearity calibration, not mentioned by Lu et al. [18,19]. Rather, strongly up-shifted LPP mode indicated high free electron concentration of $n = 2.46(2) \times 10^{18}$ cm$^{-3}$, believed to originate from dominant oxygen impurities.

The 2-D distribution of Pos(E\text{\,f})\text{\,(2)}\text{\,(4)} was confocally imaged in large 50×50 μm$^2$ c-plane area in order to estimate TD density, analyze the residual stresses and select one dislocation for a closer 3-D imaging study. Density of TDs with $\vec{\alpha}$-component of Burgers vector was estimated low $> 8 \times 10^5$ cm$^{-2}$ by counting, typically even lower for ammonothermal a-GaN. Reported phonon deformation potentials and stress-free value [19] were used to separate Pos(E\text{\,f})\text{\,(2)}\text{\,(4)} into the absolute hydrostatic and biaxial components of stress in the material, $\sigma_{02}$ and $\sigma_{11}$, respectively. The direct calculation of $\sigma_{02}$ distribution was possible due to uniform impurity concentration, which produces a constant $\sigma_{02}$ background in the material. This simplification was of high importance, because here $\sigma_{02}$ is a dominating attribute of the edge $\vec{\alpha}$-type and mixed $\vec{\alpha} + \vec{\sigma}$-type TDs. It was also argued in Section 3.2 that the screw $\vec{\alpha}$-type TD cannot be seen as Raman peak shift because it only produces shear stresses, capable of generating Raman peak split (or broadening) instead. Consequently, Pos(E\text{\,f})\text{\,(2)}\text{\,(4)} is sensitive only to the TDs with $\vec{\alpha}$-content, conclusion experimentally supported by a recent Raman study by N. Kokubo et al. (2018) [24].

Despite of being nearly three decades old technique [28], confocal Raman 3-D imaging has not yet been much used up-to-date, perhaps due to the multitude of potential error sources that can make the volumetric scan a particularly challenging task. Recent scientific and computational advances have mitigated these constraints and enabled collection of 1-D spectrum for each spatial 3-D pixel, resulting in a large hyperspectral dataset for the transparent material of interest [20,25,27]. Such large 4-D datasets demand time-consuming post-processing steps, careful analysis and some kind of dimensionality reduction, such as lineshape fitting, before they may be visualized. One dislocation was selected for such 3-D analysis, for which several 2-D maps of Lorentzian-fitted Pos(E\text{\,f})\text{\,(2)}\text{\,(4)} were collected as a function of increasing depth within smaller 3×3 μm$^2$ area. As described in Section 3.3, various precautions were taken in order to correct the dataset from many distortions and instrumental errors, such as anomalous scanline drift in Pos(E\text{\,f})\text{\,(2)}\text{\,(4)} still, it was found that the stress field dipole around the dislocation core appeared to move slightly, which was later in Section 3.4 concluded to be caused by off-center laser focusing.

Finally, this 3-D stack of images was merged into a 3-D dataset, corrected for the distortion in c-axis below the Ga-polar surface due to the abrupt change in refractive index as described in Section 2.5. Simple isosurface 3-D rendering was chosen to visualize the tensile and compressive biaxial stresses around the edge $\vec{\alpha}$-type TD in volume of $3 \times 3 \times 24.5$ μm$^3$. The dangers of misinterpreting the 3-D rendered data were emphasized in Section 3.4, few important factors being the laser point spread function convolution effect, the noise background and the potential instrumental artefacts, all of which should be taken in careful consideration. The studied dislocation was deduced to be of the edge $\vec{\alpha}$-type based on its stress field dipole and nearly zero inclination angle. Important finding from literature was that there are only six possible orientations in c-plane of stress field dipole around the TDs with edge character, understood to originate from the sixfold c-plane symmetry in the lattice. This was shown to have a strong support from various atomic-scale calculations and experiments, even though not yet much
exploited in the dislocation stress distribution studies and only directly suggested by Sintonen et al. (2014) [16] and N. Kokubo et al. (2018) [24] to authors’ best knowledge. Based on the orientation of the stress field dipole, the Burgers vector $\vec{a}$-content for the studied edge $\vec{a}$-type TD was found to be in direction of $[1\overline{1}20]$. Due to the fundamental diffraction limitation of confocal Raman microscopy, it could not be determined if it has the most common and energetically favourable 5/7-atom ring core, what should be indirectly attempted in the future studies.

The authors conclude that confocal Raman microscopy as non-destructive and stand-alone tool is very suitable for the characterization of TD types in the ammonothermally grown c-oriented bulk GaN. The 3-D imaging technique is highly recommended in order to distinguish the edge $\vec{a}$-type TD from the mixed $\vec{a} + \vec{c}$-type TD by the inclination angle and develop the understanding on their propagation and interaction in the material. Further development of the Raman peak shift, $\text{Pos}(\vec{E})^2$ analysis is needed to expand this capability to heteropitaxial $\alpha$-GaN. Obviously, more work is also needed to verify if the screw $\vec{c}$-type TD can somehow be identified by, for instance, the broadening of the Raman peak width, $\text{Fwhm}(\vec{E})^2$.

Declaration of interest

The authors declare that there is no conflict of interest.

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