Elastic Variation of Quasi-One-Dimensional Cubic-Phase GaN at Nanoscale

S. C. Lee,* E. J. Peterson,‡ Y.-B. Jiang,§ C. Wetzel,§ and S. R. J. Brueck†

†Department of Electrical and Computer Engineering and Center for High Technology Materials, University of New Mexico, Albuquerque, New Mexico 87106, United States
‡Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico 87131, United States
§Department of Physics, Applied Physics and Astronomy, Rensselaer Polytechnic Institute, Troy, New York 12180, United States

Supporting Information

ABSTRACT: The elastic properties of the cubic (c-) phase GaN confined in a nanoscale one-dimensional (1D) v-grooved Si(001) substrate are investigated. Along a ~900 nm-wide v-groove formed with two facing Si(111)-type facets, sub-micrometer-wide c-GaN is achieved by the hexagonal- to c-phase (h-c) transition from the h-GaN which plays the role of an interlayer in its epitaxy on Si. The resulting nonplanar stack of c-GaN/h-GaN on Si has complicated stress distribution. This work focuses on the elastic properties the c-GaN, which are critically affected by its low dimensionality, and presents experimental evidence for it with an analytical stress modeling. A reciprocal lattice map reveals that the c-GaN in each groove consists of several micrometer-long single crystals which are microscopically tilted from each other in their serial coalescence, as its unit structures. The corresponding micrometer-scale lateral correlation length, $d_o$, results from the h-c transition that is interrupted by the groove imperfections generated in fabrication and the stress fluctuation in the misoriented h-GaN interlayer. The modeling suggests that $d_o$ is long enough to induce the tensile stress, dominating with the longitudinal strain parallel to the groove which is ~2.5 $\times$ the transverse strain, and the c-GaN can be regarded as a serial array of a quasi-1D unit structures which retain such anisotropic stress resulting from their geometrical shape. The Poisson ratio of the c-GaN in <110> is ~0.21, close to 0.26 from a theoretical prediction. The variation of the c-phase bandgap under the given tensile stress is addressed.

INTRODUCTION

Since cubic- (c-) phase GaN was epitaxially achieved in a v-grooved Si(001) substrate by the transition from hexagonal (h-) phase GaN more than a decade ago,1,2 there have been substantial efforts to reproduce and utilize it for device applications that benefit from the advantages of c- over h-phase III–N materials.3–5 Among them, c-In$_x$Ga$_{1-x}$N/GaN quantum well (QW) light emitting diodes for green at ~500 nm wavelength without piezoelectric effects highlight its application for next generation III–N circuitry with Si technology.5,6,8

Figure 1a schematically shows the sequence of the growth for h- and c-GaN on a one-dimensional (1D) v-groove fabricated into a Si(001) substrate. As explained in the figure, it is assisted by the orientation-dependent incorporation for selective epitaxy of h-GaN inside the groove at the beginning and the phase-dependent incorporation exclusively for c-GaN immediately after critical moment of h- to c-phase (h-c) transition on a secondary v-groove by h-GaN.10

The resulting c-GaN, which is triangular in the cross section shown at Figure 1, is nm-scale in width and infinitely long in length. In the reciprocal lattice map seen later, however, it consists of several micrometer-long, single crystals as unit structures that are serially coalesced with adjacent units. This was predicted in our previous article where the spatial discontinuity in the nucleation of the c-GaN along a secondary groove by open voids on the junction of misoriented h-GaN was observed at the very initial stage.12 Then, the unit structure of the c-GaN formed along each groove should be a nanometer-scale wide, micrometer-scale long single crystal of which the geometric shape can be regarded as quasi-1D. The elastic properties of this quasi-1D c-GaN is important in photonic and electronic applications since they ultimately affect its band structure and device reliability.12,13 Evidently, its stress condition is not equivalent to that of a conventional planar, unpatterned epilayer. It is confirmed that the c-GaN in a Si v-groove is in tensile stress.5,6,7 Relying on the measurement of c-GaN on GaAs, however, it was indirectly speculated that the magnitude of the stress would be up to ~1 GPa from Raman shift and its low dimensionality has not been considered yet.2

The study on c-III-N is still not enough to analyze its material properties precisely. One of the main reasons for the data deficiency is the difficulty in growth of the c-phase which is metastable and therefore energetically less favorable than the
h-phase. In this work, we use the c-GaN spatially separated from h-GaN at large scale on a 1D v-grooved Si(001) substrate that is sufficient for materials characterization. We present a comprehensive study on the elastic properties of c-GaN with clear experimental evidence and an analytical stress modeling based on a thin mesa on a lattice-mismatched substrate. In the experiment, high-resolution (HR) X-ray diffraction (XRD) and a reciprocal lattice map (RLM) associated with it and transmission and scanning tunneling electron microscopies (TEM and STM) are employed. Owing to the low dimensionality, the unit structure of the c-GaN is under anisotropic tensile stress that is higher in the longitudinal direction parallel to the groove than the transverse direction perpendicular to it. This is quantitatively supported by the modeling with the experimental Poisson ratio close to a theoretical value. Finally, the bandgap of the c-GaN under the given stress is examined with photoluminescence (PL).

**EXPERIMENTAL SECTION**

For the fabrication of a 1D array of v-grooves on a Si(001) substrate, large-area, i-line interferometric lithography and KOH-based anisotropic chemical etching were employed. The period and width of the groove array were set to 1.8 μm and 900 nm, respectively. The details of the process are summarized elsewhere. For epitaxial growth of GaN, metal–organic vapor-phase epitaxy was used. A thin AlN film was embedded between the GaN layer and the Si substrate to assist the nucleation of GaN on the Si surface. Because of it, however, the orientation-dependent incorporation in Figure 1a was noticeably disturbed but still partially effective for the formation of the secondary v-groove by h-GaN that was critical to the h–c transition. The growth temperature was kept at ~1100 °C. Figure 1b is an SEM image of the as-grown GaN on a 1D array of v-grooves on a Si(001) substrate in bird eye’s view. The dashed lines represent the h–c boundaries in a single groove with a perspective sketch of the triangular cross section that speculates the layer structure of the c- and h-GaN inside the groove.

In XRD, the diffraction by K$_{\alpha1}$ ($= 0.15406$ nm) was considered exclusively by the curve fitting that subtracted the contribution of K$_{\alpha2}$. In this process, a pseudo-Voigt function was used. RLM was collected using a Rigaku SmartLab diffractometer equipped with a Cu-target sealed tube X-ray source, a Ge (220) two bounce incident beam monochromator, and a Rigaku D/teX position-sensitive detector. Scans were performed in continuous mode at 2° min$^{-1}$ with 0.02 deg steps.

**RESULTS AND DISCUSSION**

To measure the effects of the h-GaN interlayer in crystal orientation, the alignment of the c-GaN to the Si substrate was examined. Figure 2a is a plot of θ’s of c-GaN(002) and Si(004) versus azimuthal angle, ϕ, from HRXRD at the configuration shown in the inset which shows ϕ = 0. Figure 2b shows the rocking curves near c-GaN(002) at ϕ = 240°, as an example, with a solid red line from pseudo-Voigt fit. Thus, ϕ = 0 means the groove direction is parallel to the beam plane composed of an X-ray source and a detector. The full width at half-maximum (fwhm) of this peak ranges 12.3–13.1 arcmin for

---

**Figure 1.** (a) A schematic illustration of the growth sequence starting with a v-groove fabricated into a Si(001) substrate at the leftmost. The v-groove is filled by h- and c-GaN in the final stage at the rightmost. (b) An SEM image of the as-grown sample corresponding to the final stage in (a) at bird eye’s view. The dashed lines mean h–c boundaries. A perspective sketch of a cross section between them that reveals a layer structure is included.

**Figure 2.** (a) A plot of θ’s of c-GaN(002) (left y-axis) and Si(004) (right y-axis) versus the azimuthal angle ϕ from high-resolution XRD. Inset: A schematic configuration of measurement. (b) An HRXRD rocking curve near c-GaN(002) at ϕ = 240° (black line) with the curve fit by pseudo-Voigt function (red line). Inset: A schematic coordinate illustrating the misalignment of ($ζ$, $ϕ$) between c-GaN (green arrow) and Si in crystal axes (gray arrows).
the 360° rotation of \( \phi \). If \( \delta \theta(\phi) \) is the difference of \( \theta \) between c-GaN(002) and Si(004) at \( \phi \), Figure 2a allows us to estimate the maximum tilt angle of c-GaN with respect to the Si substrate, \( \zeta_{c} \), indicated in the inset of Figure 2b. Then, \( \zeta_{\text{max}} = \text{Max}[\delta \theta(\phi)] - \delta \theta_{0} \), where \( \delta \theta_{0} = 14.5607° \) is the reported value of the \( \delta \theta \) from bulk c-GaN \( ([= 20.0036° \text{ for (002)}]) \) and Si \( ([= 34.5643° \text{ for (004)}, \text{ Si } \approx 5048]) \). Since Max[\( \delta \theta(\phi) \)] = 14.5735° for \( \phi = 240° \), \( \zeta_{\text{max}} \) becomes 0.0128° or 46 arcsec. Here, any curvature effects by stress was not considered since the peaks were not noticeably asymmetric. In the consideration of the presence of the h-GaN interlayer in the orientation mismatch, \( \zeta_{\text{max}} \) should be taken into account in the further analysis of XRD as the maximum misalignment in the crystal orientation.

The nucleation mode observed in the c-GaN at the very early stage raises a fundamental question about its crystallinity. In this work, it was examined with RLM. Figure 3 presents the RLM from the (113) reflection of c-GaN clearly. As indicated, the intensity of the c-GaN(002) and Si(004) at \( \phi = 0° \) is at least several micrometers. Then, a quasi-1D c-GaN correlation length, \( d_{c} \), of the unit structure evolving from a single or multiple seeds in seed layers in the longitudinal direction parallel to the groove and can be interpreted as the lower bound in the length of a unit structure evolving from a single or multiple seeds in continued growth. Within \( d_{c} \), each unit structure remains single crystalline. This is very important in understanding the strain of the quasi-1D c-GaN examined below.

Figure 4 is XRD rocking curves at the configuration shown in the insets. For these measurements, the sample stage was tilted by 54.7° in \( \chi \) first and rotated with 90° step \((= 0°, 90°, 180°, \text{ and } 270°) \) in \( \phi' \). This manipulation allows us to observe c-GaN\((n=1\sim3)\) (a) along the groove \((\phi' = 0°)\) and (b) c-GaN\((h=4\sim6)\) rocking curves near c-GaN(333) for (a) \( \phi' = 0° \) and (b) \( \phi' = 90° \) at the sample stage tilted by \( \chi = 54.7° \). The X-ray is in the plane of \( \chi = 0° \). In (a), the diffraction from h-GaN(0006) is also observed. Each inset schematically shows the given \((\chi, \phi')\) configuration. In the legend of (a), ”Fit” means the sum of fitting curves for c- (light green) and h-GaN (light blue) whereas ”c-GaN\(K_{1}\)” [”h-GaN\(K_{1}\)”] means the subtraction of the contribution by \( K_{1} \) from these original fitting curves, which leaves that by \( K_{01} \) only in each curve. The same rule is applied to the c-GaN\(K_{1}\) in the legend of (b). It should be emphasized again that the fitting results do not include the \( K_{01} \) contribution in a hump at the right side of each peak since it was removed from the experimental curve before fitting to reduce the complexity expected particularly in (a). Pseudo-Voigt function was used for curve fitting.
across it ($\phi' = 90^\circ$). At $\phi' = 0$ and $180^\circ$, h-GaN(000m) ($m = 2, 4, 6$) is also observable. It has been reported that the surface roughness can affect the fwhm of a peak in a low-angle incident X-ray beam to the surface.\textsuperscript{21} In Figure 1b, the surface is relatively rough at the sub-micrometer scale. For the accuracy in fwhm, as seen in Figure 4, $n = 3$ for c-GaN and $m = 6$ for h-GaN were chosen. This removes the measurement uncertainty at low $n$ and $m$ where the angular peak separations between c- and h-GaN are too small to apply curve fitting to their analysis. For better accuracy, the Si(333) which is the closest to c-GaN(333) and h-GaN(0006) was used as the reference in stage alignment. Low $n$ diffractions which provide consistent results in peak angles will be used in Williamson-Hall (W-H) plot later for a rough estimate of the contribution of strain to fwhm.\textsuperscript{22}

The peak angle and fwhm of c-GaN(333) and h-GaN(0006) at $\phi' = 0^\circ$ in Figure 4a and $180^\circ$ (not shown), c-GaN(333) exclusively at $\phi' = 90^\circ$ in Figure 4b and $270^\circ$ (not shown), and the plane spacing calculated from them, are summarized in Table 1. Along the coordinate shown in the inset of Figure 1a, the notation of (333) for the (333)-type planes across the groove [i.e., (333) for $\phi' = 90^\circ$ and (333) for $270^\circ$] was employed for convenience to distinguish it from the other (333)-type planes along the groove [i.e., (333) for $\phi' = 0^\circ$ and (333) for $180^\circ$]. In an arithmetic average, as seen in Figure 4, the former is observed at $\theta = 62.671^\circ$, red-shifted by 0.106° from the latter at $\theta = 62.565^\circ$. This shift is significantly larger than $\zeta_{max}$. On the basis of the results in Table 1, the longitudinal strain along the unit structure and transverse strain across it (i.e., parallel to and perpendicular to the grooves), $\varepsilon_{ll}$ and $\varepsilon_{Ll}$, and the vertical strain normal to c-GaN(001) from c-GaN(002), $\varepsilon_{z}$, in Figure 2, are calculated as

\[
\begin{align*}
\varepsilon_{ll} &= 2.57 \times 10^{-3} \\
\varepsilon_{Ll} &= 9.56 \times 10^{-4} \\
\varepsilon_{z} &= -9.37 \times 10^{-4}
\end{align*}
\]  

(1)

Here, the lattice constant of unstressed c-GaN of 0.45036 nm was used.\textsuperscript{23} The details of the strain calculation were reported elsewhere.\textsuperscript{24} At eq 1, $\varepsilon_{ll}$ and $\varepsilon_{Ll}$ were obtained in [110] and [110] respectively at the coordinate in Figure 1a. Since $\varepsilon_{ll} < 0$ and both $\varepsilon_{Ll}$ and $\varepsilon_{z}$ are positive, the stress in the c-GaN must be tensile with the stress in [001] equal to zero. Then, the stresses corresponding to $\sigma_{ll}$ and $\sigma_{Ll}$, $\sigma_{ll}$, and $\sigma_{Ll}$ can be written as

\[
\sigma_{ll} = \frac{E_{110}}{(1 - \nu_{110}^2)} (\varepsilon_{ll} + \nu_{110} \varepsilon_{Ll})
\]

\[
\sigma_{Ll} = \frac{E_{110}}{(1 - \nu_{110}^2)} (\varepsilon_{Ll} + \varepsilon_{z})
\]

(2)

where $E_{110}$ and $\nu_{110}$ are Young’s modulus and Poisson ratio of c-GaN in <110> respectively. Here, the identical Poisson ratio for both longitudinal and transverse directions was assumed from the elastic properties of pattern-free c-GaN. Since $\varepsilon_{ll} = -(\nu_{110}/E_{110})(\sigma_{ll} + \sigma_{Ll}) = -\nu_{110}(\varepsilon_{ll} + \varepsilon_{Ll})/(1 - \nu_{110})$ by eq 2, $\nu_{110} = 0.210$ from eq 1. Then, the ratio of $\sigma_{ll}$ to $\sigma_{Ll}$, $\rho$, becomes 1.85 from eq 2.

In cubic crystals, the Young’s modulus and Poisson ratio in [hkI], $E_{hkI}$ and $\nu_{hkI}$ are written as

\[
E_{hkI} = \frac{s_{11} - 2(n_{11} - n_{12}) - \frac{1}{2} (s_{44})}{(s_{11})^2 + k^2 + l^2 + m^2}
\]

\[
\nu_{hkI} = \frac{1}{2} - \frac{E_{hkI}(n_{11} + 2n_{12})}{E_{110}}
\]

where $s_{11} (= 0.005521)$, $s_{12} (= -0.001942)$, and $s_{44} (= 0.006452)$ are the compliances of a given material assumed to have the stiffness coefficients reported in theoretical modeling of c-GaN.\textsuperscript{25} Using these results, $E_{110}^{th} = 293$ GPa and $\nu_{110}^{th} = 0.260$, close to the experimental $\nu_{110}$, were obtained. It should be noted that $E_{110}^{th} > E_{001}^{th} = 181$ GPa and $\nu_{110}^{th} < \nu_{001}^{th} = 0.352$ implying anisotropic elasticity in unstressed c-GaN, where the subscript of 001 corresponds to <001>. Applying $E_{110}^{th}$ and $\nu_{110}^{th}$ to eq 2 with the strains in eq 1, $\sigma_{ll}^{th} = 0.886$ GPa and $\sigma_{Ll}^{th} = 0.510$ GPa, leading to $\sigma_{ll}^{th}/\sigma_{Ll}^{th} = 1.74$. This is not very different from the $\rho = 1.85$ of the experiment but examined with further discussion presented below.

If $\nu_{110} = 0.210$ from the experiment and $E_{110}^{th}$ are applied to eq 2 with the strains in eq 1, $\sigma_{ll} = 0.85$ GPa and $\sigma_{Ll} = 0.46$ GPa, which are used in the calculation of the strains, the strain ratios obtained from this phenomenological approach are rough. Thus, the stresses obtained from this phenomenological approach are reliable. Then, it can be concluded that the c-GaN epitaxially confined in a 1D groove is in a tensile stress of $\sim0.85$ GPa longitudinally along the unit structure and $\sim0.46$ GPa transversely across it. This means the stress is anisotropic and is affected by the low dimensionality in the geometrical shape of the unit structure of the c-GaN.

The stress obtained with eqs 1 and 2 is crucial in the design of electronic states of low-dimensional structures such as QWs and quantum wires if the III–V’s from the h~N transition on a v-groove are employed for the targeted emission or absorption of photons through the transition between those states. Basically, the stress in an epilayer induces a change of bandgap.\textsuperscript{26} It reduces the degeneracy of heavy- and light-hole states at the bandgap of most semiconductors including III–V that affects their fundamental electronic and optical properties. The anisotropic biaxial stress observed in this work entangles the band structure with high complexity. Particularly, this could be very critical to the inter-subband transitions for long wavelength infrared and THz applications in the low dimensional structures where a minor change of individual electronic states results in a relatively large shift in emission and absorption at this range.\textsuperscript{27,28} In this work, the

\[
\text{DOI: 10.1021/acs.cgd.9b00339}
\]

Crystal Growth & Design

5049


Table 1. Summary of XRD Results

<table>
<thead>
<tr>
<th>$\phi'$ (deg)</th>
<th>0</th>
<th>90</th>
<th>180</th>
<th>270</th>
</tr>
</thead>
<tbody>
<tr>
<td>c-GaN(333)</td>
<td>peak (θ)</td>
<td>62.680</td>
<td>62.568</td>
<td>62.682</td>
</tr>
<tr>
<td>d$_{333}$ (nm)</td>
<td>0.08672</td>
<td>0.08679</td>
<td>0.08670</td>
<td>0.08679</td>
</tr>
<tr>
<td>fwhm (deg)</td>
<td>0.267</td>
<td>0.330</td>
<td>0.272</td>
<td>0.370</td>
</tr>
<tr>
<td>h-GaN(0006)</td>
<td>peak (θ)</td>
<td>63.016</td>
<td>not available</td>
<td>63.018</td>
</tr>
<tr>
<td>d$_{001}$ (nm)</td>
<td>0.86440</td>
<td>0.86438</td>
<td></td>
<td></td>
</tr>
<tr>
<td>fwhm (deg)</td>
<td>0.317</td>
<td>0.357</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
anisotropic stress on the c-GaN with \( \rho = 1.85 \) primarily depends on the 1D groove. The experimental results then can be compared with a stress modeling of a rectangular mesa film lattice-mismatched to a substrate. The inset of Figure 5 schematically shows the structure used in the stress modeling that consists of a mesa film (length, \( d \); width, \( w \); thickness, \( t \)) on a substrate. Relying on the formalism based on Hu’s model that was proposed to simulate the stress variation near the edge of a film, the ratio of stress along \( d \) to that along \( w \) at the center of the film, \( \rho_m \), can be analytically expressed as

\[
\rho_m \left( \frac{d}{2}, \frac{w}{2}, \frac{t}{2} \right) = \frac{1 - 2\varepsilon - \sqrt{3Kd/w}}{1 - 2\varepsilon - \sqrt{3Kw/d}}
\]

(3)

where \( K = E_s(1 - \nu_s^2)/E_f(1 - \nu_f^2) \) with the Young’s modulus and Poisson ratio of the substrate (film), \( E_s (E_f) \) and \( \nu_s (\nu_f) \), respectively. From the typical dimension of the c-GaN of \( w \approx 700 \) nm and \( t \approx 250 \) nm for an effective mesa shape in Figure 1, the \( \rho_m \) of eq 3 becomes a function of \( d \) that can converge to \( \sim 1.85 \) as \( d \to \infty \) for matching the experimental \( \rho \) measured earlier since the apparent \( d/w \) of the c-GaN confined in a groove is not small. Figure 5 is a plot of \( \rho_m \) versus \( d/w \) for the given \( w \) and \( t \) with \( K \) as a parameter ranging from 1 to 1.5. Evidently, \( \rho_m = 1 \) for \( d/w = 1 \) regardless of \( K \) and does not depend on the misfit between film and substrate explicitly since it is only a ratio of stresses. In Figure 5, \( \rho_m \) shows noticeable change with \( d/w \) particularly at its small value near 1. On the other hand, its convergence for \( d \to \infty \) is determined by \( K \); \( K = 1.214 \) for \( \rho_m = \rho = 1.85 \) at \( d \to \infty \). At this value, \( \rho_m \geq \rho \) within 1% error for \( d/w > 14 \), meaning \( d \geq 10 \) \( \mu \)m, and the minimum length compatible with the experimental \( \rho \) at the given \( w \) in this modeling, \( d_m \), is then \( \sim 10 \) \( \mu \)m. It should be noted that the \( d_c \) obtained from Figure 3 does not contradict this \( d_m \). While more rigorous approaches is required for better understanding of pattern-induced strain, the \( \rho_m \) of eq 3

Figure 5. A plot of \( \rho_m \) vs \( d/w \) of the film shown in the inset that is calculated by eq 3 with the variation of \( K \). The dashed line means \( \rho_m = 1.85 \).
conceptually explains the anisotropic biaxial stress observed from the c-GaN consisting of μm-scale, quasi-1D unit structures in spite of different layer structure assumed in the modeling. Further analysis for K available with the modeling is presented in the Supporting Information.

On the basis of the interpretation of the experimental results in our previous work, we proposed that the v-groove width available for the h→c transition could be limited by the migration length of Ga adatoms on the secondary v-groove at a given growth condition.18 While the migration of Ga adatoms depends on several growth parameters such as growth temperature, deposition rate, III/N flux ratio, and on the orientation of growth front surface, we have speculated the adatom surface migration length of a few micrometers on GaN based on typical III–V epitaxy since no reliable data for c-III–N have been reported yet. Under this condition, the largest groove width available for the c–III-N (or the maximal w in the model of Figure 5) would be increased up to several micrometers, which then becomes comparable to the d_c of its unit structure if the identical h→c transition is assumed. Eventually, the d_w corresponding to a wider v-groove would approach 1 in Figure 5 at this condition and the c-GaN should be closer to isotropic, biaxial stress. Further research is required to examine the validity of the model at the scale-up of the w ≈ d_c observed in this work and another extreme case of w → 0.

In a heterolayered structure, the critical thickness of each layer is impacted by the lattice mismatch between constituting materials. For example, the critical thickness of c-GaN on a MgO substrate from the precise in situ measurement of strain relaxation during epitaxy was only a few monolayers as a result of the large lattice mismatch of ~0.07.31 Since c-GaN has a lattice mismatch to Si of ~0.17, considerably greater than this value, its direct, unpatterned epitaxy on Si will be seriously perturbed from the beginning of the nucleation. In the c-GaN examined in this work, however, most of the defects associated with the lattice- and phase-mismatch were quenched through the h-GaN interlayer of which the nucleation is locally favorable on the (111) facets at the given patterned Si substrate. Figure 6 shows TEM, SEM, and STM images of the c-GaN/h-GaN on a Si(001) substrate taken (a) across and (b) along the groove. The physical dimension of the c-GaN is indicated in Figure 6a. In Figure 6b, the middle panel passes through the center of the groove in the SEM image at the top panel (dot-dashed line) within ±50 nm. In selected area electron diffraction along the distance over several d_c’s (not shown) as well as both high- and low-resolution TEM and STM, no imperfections such as antiphase defects or crystal misorientations that could be suspected as the boundaries between unit structures were observed clearly. At the moment of the coalescence in continued epitaxy, however, the formation of such imperfections is inevitable. The finite Δφ observed in RLM is more evidence for it. This is very important in understanding the characteristics of the c-GaN from the h→c transition in the given patterned epitaxy.

Together with Figure 1b, Figure 6 also reveals that the top surface of c-GaN is not very flat but degraded by faceting and undulation along the groove. The surface undulation observed in Figure 6b occurs unidirectionally in a longitudinal direction with a sub-micrometer-scale period, whereas its amplitude in the STM image at the bottom does not exceed ~100 nm. It is known that surface undulation increases the total surface area per unit area and leads to partial relief of strain energy.35 The rough c-GaN surface that includes faceting as well as undulation could be partly related to its initial island-type nucleation mode analogous to the self-assembly of conventional quantum dots but eventually contributes to the strain relief in the longitudinal direction. These emphasize the significance of the c-GaN heteroepitaxy from a single nanodot proposed in our previous work that can resolve surface morphology as well as microscopic tilt.11

In Figure 6b,c, STM and dark-field TEM show the details of both c- and h-GaN in crystallinity along the center of the groove; h-GaN is highly defected—its crystal axes off to the cross section make the image quality worse—whereas c-GaN is much improved. However, c-GaN suffers from a large number of stacking faults (SFs) as confirmed in both cross sections. As an example, the high-resolution TEM in Figure 6c focuses on a bunch of SFs in the c-GaN that extends to the top surface. Even some defects indicated by the arrows in the dark-field TEM image in Figure 6c look to have the origin in the h-GaN. In XRD, SF is a major cause of peak broadening.33 As seen in Table 1, the fwhm’s of c-GaN(333) at φ|| = 90° and 270° for ε|| (~21 arcmin) are persistently greater than those at φ|| = 0° and 180° for ε⊥ (~16 arcmin), while ε|| > ε⊥ in eq 1. A W–H plot provides a rough idea for the SF spacing, d_SF, and the strain associated with fwhm. It suggests that the fwhm of c-GaN(333) greater than that of c-GaN(333) by more than 30% can be interpreted mostly with the larger longitudinal strain and then d_SF ≈ 50 ± 5 nm. Here, d_SF is regarded as the lower limit of average SF spacing by assuming that SFs dominantly contribute to fwhm among the crystal defects in the c-GaN. The details of the W–H plot for the d_SF obtained from the c-GaN are summarized in the Supporting Information. The d_SF is compatible with the upper limit of ~100 nm observed at the initial stage of the c-GaN, which was grown under similar conditions.11 This means the SFs observed in the c-GaN are mostly generated at the beginning of its nucleation.

Despite a high SF density, the c-GaN in each groove retains tensile stress. It should be noted that the fault of the stacking in c-GaN means the order of stacking that can exactly match h-GaN. This implies the SF formation in the metastable c-GaN could be regarded as a process driving the epitaxy to a lower energy state by local formation of stable h-GaN. Rather than generating dislocations that require a certain activation energy which should be greater than that of an SF, the c-GaN in the groove array can reduce its excessive strain energy with SFs. As observed earlier, d_c ≈ d_m is also consistent with the sub-micrometer period, unidirectional surface undulation observed in Figures 1b and 6b that contributes to the partial relief of the stress within d_c. From the comparison of d_c with these lengths, therefore, a c-GaN nucleus (or a 1D seed layer) is homogeneously initiated along the bottom of the secondary h-GaN v-groove with micrometer-scale d_c at the moment of the h→c phase transition. Also, the stress built at each unit structure evolving from the seeds in continued growth is higher in longitudinal than transverse direction by its low-dimensional geometric shape but partially relieved with SFs and surface undulation.

In the inset of Figure 3, the (113) reflection from the c-GaN is slightly above that from the Si substrate (the peak off from the dashed line); the 25.25° of the Si(113) reflection is greater than the 25.20° of the c-GaN(113) reflection by 0.05°. In the q_400 plot of RLM shown in Figure 3, the (113) reflection from the c-GaN has the peak at (0.3139 Å⁻¹, 0.6669 Å⁻¹), which is
observed: a narrow strong peak at 3.197 eV and the other broad peak around 2.8 eV. The former has an energy very close to the bandgap of c-GaN. It may not be an exciton-related transition since the defect density is not low in the c-GaN. However, the absence of h-GaN related peaks around 3.4 eV implies that the c-GaN at the surface dominates the PL at room temperature.26,35 It is comparable to but slightly lower than the peak energy of the planar and patterned c-GaN grown on SiC ranging 3.200–3.222 eV.35 More red shift of the PL peak can imply higher tensile stress,2,26 and the c-GaN of this work could be then in the stress greater than that on SiC in PL and indirectly confirms the tensile stress observed in XRD. Ultimately, the anisotropic stress of the c-GaN confined in a 1D groove from XRD and PL emphasizes its significance for the electronic properties that must be counted in the design of low-dimensional III–N devices. The latter so-called blue luminescence at ~2.8 eV could be defect-related transitions that have been reported previously.36,37 In energy, this peak is very similar to that reported recently, which was interpreted as the donor-to-acceptor transition originated from a nominally undoped c-GaN by the h–c transition.36,38

SUMMARY AND CONCLUSION
The elastic properties of the c-GaN which are affected by low dimensional geometric shape have been reported. The c-GaN consists of ~700 nm-wide, micrometer-scale-long, quasi-1D single crystals as unit structures, which are in tensile stress keeping the longitudinal strain of $2.57 \times 10^{-3}$ along [110], parallel to the v-groove. This is almost 2.5× the transverse strain. Relying on the anisotropy of elastic properties and Young’s modulus from a model, the ratio of the longitudinal to the transverse stress of ~1.85 in a unit structure has been measured. This anisotropic stress to a unit structure is induced from its low dimensionality that is supported by an analytical modeling. The Poisson ratio of the c-GaN of ~0.210 in <110>, close to a theoretical value of 0.26, was obtained at the given structure. In each unit structure, stacking faults and unidirectional surface undulation contribute to the partial relief of excessive strain energy with no dislocations. A slight red-shift of band-to-band PL was interpreted as indirect evidence for the tensile stress on it. Conclusively, the elastic properties of the c-GaN confined in a 1D groove have been experimentally investigated, and its anisotropic characteristics by quasi-1D geometric shape associated with the nucleation mode must be considered in the design of the c-III–N photonic and electronic devices on Si.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.9b00339.

Reciprocal lattice map of c-GaN, discussion on K of eq 3, W−H plot of c-GaN (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: sclee@chtm.unm.edu.

ORCID

S. C. Lee: 0000-0003-3283-6016

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was primarily supported by the Engineering Research Centers Program (ERC) of the National Science Foundation under NSF Cooperative Agreement No. EEC-0812056.

REFERENCES

Barriers.


(16) In this work, only $\xi_{\text{max}}$ was estimated. As indicated in the inset of Figure 2b, the rotation angle of the $c$-GaN[001] to Si[001], $\phi$, should be also considered for the exact specification of the crystalline axes of the c-GaN. Since $\xi_{\text{max}}$ is too small, the maximum of $\phi$ would not be noticeable, as confirmed by TEM.


(34) It is not clear whether the fine structure in this peak ($3.197$ eV and the bump on its high energy side at $3.24$ eV) is related to the splitting of the heavy- and light-hole of the valence band in the c-GaN under the biaxial stress predicted in ref 26. A more rigorous study is required to understand it.

(35) Kemper, R. M.; As, D. J.; Lindner, J. K. N. Silicon-Based Nanomaterials; Li, H., Ed.; Springer: New York, 2013; Chapter 15.

