Nondestructive visualization of threading dislocations in GaN by micro raman mapping

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Threaded dislocations (TDs) in a HVPE-grown c-plane (0001) GaN single crystal were analyzed by micro Raman spectroscopy mapping. The mapping image exhibited the pairs of higher and lower wavenumber regions of $E_2^\text{LO}$ peak shift of GaN, which corresponded to the compressive and tensile strains due to TDs. By comparing X-ray topography and etch pit images, the contrasts are considered as the edge component of TDs. By analyzing the existing 290 TDs in $80 \times 80 \mu m^2$, the directions of the contrast were mainly dominant toward (1120). A few brighter contrasts toward (1120) were also observed. These TDs are affiliated with Burgers vectors $b = a/3(1120)$, and $b = a (01\bar{1}0)$, respectively. Judging from experimental and simulated result, it is confirmed that the contrast in the Raman mapping image of the $b = a (01\bar{1}0)$ has a larger magnitude than the $b = a/3(1120)$. © 2019 The Japan Society of Applied Physics

1. Introduction

Wide-band-gap semiconductors, silicon carbide (SiC) and gallium nitride (GaN), have attracted considerable attention as next-generation power semiconductor materials because of high-temperature operation owing to its large band-gap and low intrinsic carrier density. SiC-based power device has started mass production with 150 mm wafers. Although state of the arts hydride vapor-phase epitaxy (HVPE)-grown freestanding GaN substrates have become commercially available, the size is only 50 mm and their dislocation densities are still on standing GaN substrates have become commercially available, of the arts hydride vapor-phase epitaxy (HVPE)-grown free-standing GaN substrates have become commercially available, state of the arts hydride vapor-phase epitaxy (HVPE)-grown freestanding GaN substrates have become commercially available, have become commercially available, of the arts hydride vapor-phase epitaxy (HVPE)-grown free-standing GaN substrates have become commercially available. Although GaN substrates contain threading dislocations (TDs), those of which are composed of threading screw dislocations (TSDs), threading edge dislocations (TEDs), and threading mixed dislocations (TMDs). The TSDs, TEDs, and TMDs have dislocations propagating to the $c$-axis with Burgers vectors of $b = c (0001)$, $a/3 (1120)$, and $c (0001) + a/3 (1120)$, respectively. It is important to characterize the TDs in GaN crystals because the device performance would be affected by existence of the TDs.

Several evaluation methods for TDs in GaN crystals are proposed, such as chemical etching, transmission electron microscopy (TEM), X-ray topography, cathodoluminescence (CL), and photoluminescence (PL). Among them, the chemical etching of GaN bulk crystals is commonly used: however, classification of the dislocations is relatively difficult because the shape of the etch pits depends on theetching conditions and crystal manufacturing methods. TEM can determine the Burgers vector of dislocations; however, the sample must be thinned into a thickness of several 100 nm, which requires time and destructive process. The X-ray topography is usually used as a nondestructive characterization method for determination of the direction of the Burgers vector of TMDs and TSDs in GaN crystals; however, a synchrotron radiation facility is required to obtain clear contrast images. CL mapping measurements can identify the location of dislocations; however, they must be performed under vacuum conditions. The three-dimensional imaging of TDs in GaN films was recently visualized by two-photon excitation PL without any destructive preparations.

We proposed the micro Raman spectroscopy mapping as a nondestructive characterization method for evaluation of TDs in GaN. In the commercially available GaN freestanding substrates, the densities and types of the TDs would vary between wafer vendors. It is unrealistic to determine the direction and magnitude of Burgers vectors for all TDs by TEM. By analyzing the Raman mapping of the $E_2^\text{LO}$ peak shift within 0.1 cm$^{-1}$ range, the density, direction, and magnitude of the edge component of the TDs were determined. In this study, we analyzed the direction of the $E_2^\text{LO}$ peak shift from Raman spectroscopy mapping images for 290 TDs. By comparing computer simulation, we found that almost all TDs were composed Burgers vectors of $b = a/3 (1120)$, a few TDs were composed of $b = a (01\bar{1}0)$.

2. Experimental

A HVPE-grown c-plane GaN substrate, produced by Nanowin, was used as the evaluation sample. The thickness and density of the TDs were 350 $\mu$m and ~10$^5$ cm$^{-2}$, respectively. Raman scattering spectroscopy measurements were performed at RT using an in-Via Raman system (RENSHAW). To increase the wavenumber resolution, the 532 nm laser intensity was maximized ~150 mW and the grating width of 3000 gl mm$^{-1}$ was selected. An objective lens with a magnification of 100 times and a high numerical aperture of 0.85 were used. The theoretical minimum spot size and excitation power density were estimated to be 0.76 $\mu$m and 33 MW cm$^{-2}$, respectively. The laser was focused at 1.0 $\mu$m depth from the surface and the depth range of focus was calculated as $\pm 0.86 \mu$m. The irradiation time and integration number were 0.2 s and 1, respectively.
A step width of 0.3 μm was applied to increase the spatial resolution. The wavenumber resolution at the detector was estimated to be 0.8 cm⁻¹. For data analysis, the Raman software WIRE 3.4 (made by RENISHAW) was used.

X-ray topography was conducted at the beam line of BL8S2 in Aichi Synchrotron Optical Center. The diffracted X-rays were imaged on a nuclear dry plate. In X-ray topography, the diffraction planes of g = 0006 was used. The penetration depth of the g = 0006 was estimated to be t₀₀₀₆ = 15.78 μm. The etch pit formation of GaN substrate was chemically etched by a KOH in the Ni crucible at 500 °C for 15 min. After the etching, the surface of GaN were observed by optical microscope.

The simulation of Raman mapping is based on the theory of elasticity. The strain field (εᵢ) around the TD in the GaN crystals is calculated by using the elastic compliance constant (Sᵢⱼ) and the stress field (σᵢ) by Fook's law under elastic continuum approximation considering six-fold symmetry

\[ εᵢ = \sum_j Sᵢⱼ σⱼ, \]

\[ Sᵢⱼ = \begin{bmatrix} S₁₁ & S₁₂ & S₁₃ & 0 & 0 & 0 \\ S₁₂ & S₁₁ & S₁₃ & 0 & 0 & 0 \\ S₁₃ & S₁₃ & S₁₁ & 0 & 0 & 0 \\ 0 & 0 & 0 & S₄₄ & 0 & 0 \\ 0 & 0 & 0 & 0 & S₄₄ & 0 \\ 0 & 0 & 0 & 0 & 0 & S₆₆ \end{bmatrix}. \]

We applied S₁₁ = 390, S₁₂ = 145, S₁₃ = 106, S₃₃ = 398, S₄₄ = 105, and S₆₆ = 122.5 (GPa). Additionally, the lattice constants a = 0.319 nm and c = 0.519 nm were adopted. Fig. 1 shows a typical Raman spectrum of the c-plane (0001) n-type GaN single crystal. The three peaks are observed at 145.0, 567.8, and 734.2 cm⁻¹, which are labeled as E₂², E₃², and A₁(LO), respectively. Both the E₂² and E₃² is a transverse optical mode while the A₁(LO) is a longitudinal optical mode in which atoms are displaced in a plane perpendicular to the c-axis. The E₂² peak shift (Δω_E₂²) in Raman scattering is expressed by the following equations:

\[ \Delta ω_E₂² = a_E₂²(ε_{xx} + ε_{yy}) + b_E₂²ε_{zz}. \]

Here, the deformation potential constants of \( a_E₂² = -850 \) (cm⁻¹), \( b_E₂² = -920 \) (cm⁻¹) were used. By this conversion, the distribution of the peak shifts was calculated. The Raman mapping image was created by calculating the peak shift at each point with a 0.3 μm step. The detailed simulation procedure will be reported in a separate paper.

3. Results and discussion

3.1. Comparing etch pit, X-ray topography, and Raman mapping images

Figure 2(a) shows an etch pit image of the GaN single crystal (100 × 100 μm²). Two different contrasts (black and white hexagonal shape) are clearly observed. The black ones have the densities of 2.6 × 10⁷ cm⁻² and are considered as the TDs. In contrast, the white ones are not related to the TDs since there is no core from depth profile (not shown). In our etching condition, it is difficult to classify TDs into TEDs, TSDs, and TMDs. Figure 2(b) shows an X-ray topography image along the g = 0006 diffraction at the same location. It should be noted that the X-ray topography was measured before etch pit formation. In the X-ray topography image along the g = 0006, the TSDs and TMDs are observed as bright dot-like contrast. The TEDs cannot be observed in the g = 0006 diffraction due to g · b = 0.

In the Raman mapping contrast image of the E₂² peak shift in Fig. 2(c), the white (higher wavenumber) and the black (lower wavenumber) regions are clearly observed. It is noteworthy that the wavenumber resolution at the detector was estimated to be 0.8 cm⁻¹, change in E₂² peak shift within 0.1 cm⁻¹ range is detected. We insist very slight peak shift can be discussed by peak fitting using Voigt function. When an isotropic compressive strain is applied to the GaN crystal, the E₂² peak is shifted to the higher wavenumbers and a tensile strain results in the lower wavenumbers. Therefore, it is considered that compressive strain and tensile strain are present as a pair at a place where contrast appears, which can be addressed as the TEDs and TMDs. As already reported, the TSDs do not affect the E₂² peak shift. Comparing the contrast spot in Figs. 2(b) and 2(c), the TEDs and TMDs are classified as red arrows and green arrows, respectively. The density of the TEDs and TMDs are then counted as 1.0 × 10⁵ cm⁻² and 1.3 × 10⁵ cm⁻², respectively. The density of the TSD is estimated to be less than 1.0 × 10⁵ cm⁻² because there is no TSDs in the 100 × 100 μm² scan area.

3.2. The direction of the edge-component Burgers vector in GaN crystal

Figure 3(a) shows a typical Raman mapping image of the E₂² peak shift of 80 × 80 μm². Here, the direction from the white (higher wavenumber) to the black (lower wavenumber) regions is indicated by the white dotted arrow. As seen in Fig. 3(b), the directions are recognized as the GaN wurtzite crystal orientations, [01T0], [1T00], [10T0], [0110], [1100], and [10T0]. Figure 3(c) shows histograms of azimuthal distribution of the E₂² peak shift for 290 TDs. It is clearly observed that six groups of peaks at 30°, 90°, 150°, 210°, 270°, and 330° (60 n + 30°, n = 0 ~ 5) from [1120]. The distribution of each group has ±15° distribution, which is probably caused by an insufficient resolution of current Raman scattering setup. These contrasts, such as the TD-B (90°, [1100]) and TD-C (150°, [1010]), are relatively weak. On the other hand, the contrast of the TD-A (120°, [2110])
shows clearer. Figure 4(a) illustrates schematic of GaN crystal structure. It is easily understood that the crystal consists from the synthesis of $\{0110\}$ and $\{1120\}$ and $\{1210\}$.

Figure 4(b) shows the simulation result for the Raman mapping images of the $E_2^H$ peak shift of the TD-A, TD-B, and TD-C with different Burgers vectors of $\mathbf{b} = a[01\overline{1}0]$, $a/3[\overline{1}1\overline{2}0]$, and $a/3[\overline{1}2\overline{1}0]$, respectively. It is clearly seen the directions from the higher wavenumber region to the lower wavenumber region are found to be in the $90^\circ$ rotation from the Burgers vectors. The directions of the contrast by simulation agree with experimental result. Therefore, the direction of the edge component of the TD can be identified by analyzing the Raman mapping image.

3.3. The magnitude of the edge-component Burgers vector in GaN crystal

In order to discuss the magnitude of Burgers vector of TDs, the $E_2^H$ peak shift of the TD-A and TD-B were compared. From experimental Raman mapping image of the $E_2^H$ peak shift for the TD-A and TD-B [Figs. 5(a) and 5(b), respectively], the line profile of the $E_2^H$ peak shift is extracted as in Fig. 5(c). Both the TD-A and TD-B shows gradual decrease in $E_2^H$ peak shift toward the TD, then an abrupt change at the center of TDs, and a gradual decrease toward the edges. The maximum $E_2^H$ peak shifts for the TD-A and TD-B are $\pm 0.03$ and $\pm 0.02$ cm$^{-1}$, respectively. The results indicate that the Burgers vectors of the TD-A and TD-B have different magnitudes. The simulation Raman mapping images are shown in Figs. 5(d) and 5(e) with Burgers vector of $\mathbf{b} = a[\overline{1}1\overline{0}0]$ and $\mathbf{b} = a/3[\overline{1}1\overline{2}0]$, respectively. Figure 5(f) shows the extracted line profiles of the simulated $E_2^H$ peak shift with Burgers vector of $\mathbf{b} = a[01\overline{1}0]$ and $\mathbf{b} = a/3[\overline{1}1\overline{2}0]$. When the magnitude of the Burgers vector of $a/3[\overline{1}1\overline{2}0]$ was multiplied by $\sqrt{3}$, larger strain occurred, and the contrast of the peak shift became clearer. The maximum $E_2^H$ peak shifts for Figs. 5(d) and 5(e) are $\pm 0.05$
Simulated Raman mapping images of the $E_{2}^{H}$ peak shift. By analyzing the existing 290 TDs in 80 images, the contrasts are considered as the edge component of TDs. The location of contrast spots of the TED and TMD were agreed with that of the etch pit image. The location and the density of the TED and TMD were classified by comparing the X-ray topography image along the $g = 0006$. By comparing X-ray topography and etch pit images, the contrasts are considered as the edge component of TDs. By analyzing the existing 290 TDs in $80 \times 80 \mu m^2$, the directions of the contrast were mainly dominant toward (1010). A few brighter contrasts toward (1120) were also observed. These TDs are affiliated with Burgers vectors of $b = a/3(1120)$, and $b = a/2(0110)$, respectively. Judging from the experimental and simulated result, it is confirmed that the contrast in Raman mapping image of $b = a/2(0110)$ has a larger magnitude than the $b = a/3(1120)$.

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