Breakdown of the Selection Rule of Raman Spectra in a Single GaN Nanocolumn

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We study micro-Raman spectroscopy in free-standing single GaN nanocolumns with 0.45-2.1 µm diameters, which are synthesized by rf-plasma-assisted molecular beam epitaxy. We clearly observe the breakdown of the polarization selection rule of Raman spectra from $E_2^\text{TO}$ phonon, when the diameter of nanocolumn is thinner than four times the wavelength of incident light inside the sample. The selection rule gets recovered with increasing diameter of nanocolumn. Moreover, we observe quasi-TO phonon modes, which strongly affects the Raman spectra from the $A_1$(TO) and $E_1$(TO) phonons. [DOI: 10.1930/ejssnt.2012.321]

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I. INTRODUCTION

Recently, nanosized materials have aroused great attention because of application to devices and mesoscopic research. Gallium nitride is a promising semiconductor material for optoelectronic applications, in particular laser diodes emitting light in the blue and green frequency range. The semiconductor one-dimensional (1D) nanostructures, which are named nanocolumns, nanowires, nanorods, or nanopillars, feature a low density of structure defects and are, therefore, ideally suited for optoelectronic nanodevices. Moreover, their high surface-to-volume ratio and high aspect ratios result in significant changes in their optical properties when compared with those of bulk materials.

Yoshizawa et al. [1, 2] first succeeded in growing GaN columnar nanostructure, i.e., GaN nanocolumns on (0001) Al$_2$O$_3$ by rf-plasma-assisted molecular beam epitaxy (rf-MBE) through a self-organization process. They reported that the photoluminescence intensity in the GaN nanocolumns was 20-30 times stronger than that in GaN continuous film grown by metalorganic chemical vapor deposition (MOCVD) because the former structures are almost dislocation-free and the surface non-radiative recombination rate is very low [3]. Recently, the regularly-arrayed GaN nanocolumns were fabricated by using pre-deposited Ti nanopatterns on the GaN templates deposited on the Al$_2$O$_3$ substrate [4].

However, despite rapid developments in the fabrications of GaN-based nanostructures, many fundamental properties of the nanostructures are not fully understood yet. The characterization of physical properties of the nanostructures, in particular the single nanocolumn is still a challenge for fundamental science and advanced technology.

Raman scattering is a powerful method to study lattice dynamics in the nanostructures, in particular to study how the phonon properties are affected by the finite size of the crystal. Recently, Schäfer-Nolte et al. [5] studied Raman scattering in single GaN nanowires with diameters of 50-90 nm and found that Raman spectra from phonon modes are governed by the sized finite effect rather than the selection rules of the wurtzite structure. It is probably inferred from the fact that the internal field polarized perpendicular to the nanowire axis is attenuated with respect to the external field for a cylindrical nanowire with a diameter much smaller than the wavelength of the excitation light [6, 7]. Meanwhile, Livneh et al. [8] reported that the Raman intensities from phonon modes were determined by the complex-valued Raman tensors, but no effect of the finite crystal size was observed in a single nanowire of 500-nm diameter. On the other hand, Hsiao et al. [9] performed orientation-dependent Raman measurement on single GaN nanorods and verified that the Raman selection rules in single nanorods were determined by the real-valued Raman tensors and still follow those of bulk GaN.

The polarization selection rule of phonon Raman scattering in the GaN nanowires or nanocolumns is still controversial. Then we study the selection rule of Raman spectra in isolated single GaN nanocolumns with various diameters in this report.

II. EXPERIMENTAL

A large assemblage of undoped GaN nanocolumns with hexagonal wurtzite crystal structures is grown by rf-MBE method, which uses rf-plasma-excited nitrogen, on n-type Si substrate [1, 2]. These are grown along the $c$ crystal axis, i.e., the [0001] direction at high density of about $10^9$-$10^{10}$ columns/cm$^2$. The assemblage of GaN nanocolumns was sonicated from the growth substrate in dichloroethane solution, and individual GaN nanocolumns possessing 0.45-1.1 µm diameters and about 12 µm length were dispersed onto sapphire substrates. A sample with a 2.1-µm diameter was made from the regularly-arrayed GaN nanocolumns [4]. The hexagonal nanocolumns have well defined facets of {1100} planes, but the 2π/3 corners are a little bit rounded.

Raman spectra were mainly excited with a backscatter-
FIG. 1: The dependence of Raman spectrum of a single GaN nanocolumn with a 450-nm diameter. The blue solid curve denotes the fitting, the blue dashed curves its four components, and the blue dashed line the background.

ing configuration on the \(x\) crystal surface, i.e., the \((1100)\) crystal plane, which is normal to the \(z(c)\) one. We used the 532.0-nm line of diode pumped solid state laser as an excitation source. The laser beam with a pot size of \(z\) direction by rotating the sample. The polarization of the scattered light is set parallel to that of a single GaN nanocolumn with a 450-nm diameter. The laser light is incident on the \((1\bar{1}00)\) crystal plane, there is a possibility that it is also incident on the \((1\bar{1}0)\) plane in thin nanocolumns. The Raman spectrum is dispersed by a triple grating spectrometer (Jovin-Yvon T64000), and detected with a cooled CCD detector.

\[\begin{align*}
R^1(E_2^{\text{H}}) &= \begin{pmatrix} d & 0 & 0 \\ 0 & -d & 0 \\ 0 & 0 & 0 \end{pmatrix}, \\
R^2(E_2^{\text{H}}) &= \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.
\end{align*}\]

III. RESULTS AND DISCUSSION

Figure 1 shows the dependence of Raman spectrum of a single GaN nanocolumn with a 450-nm diameter. The polarization of the scattered light is set parallel to that of the incident light. We changed the polarization direction \(\theta\) from the \(z(c)\) crystal axis to the \(y\) one, i.e., to the \([1120]\) direction by rotating the sample.

We observed four peaks between 500 and 580 cm\(^{-1}\). There are an \(A_1\), an \(E_1\), and two \(E_2\) Raman-active optical phonon modes in wurtzite GaN, and the \(A_1\) and \(E_1\) modes are split into transverse optical (TO) and longitudinal optical (LO) modes by electromagnetic fields, respectively. The peaks at 530, 557, and 565 cm\(^{-1}\) are attributed to the \(A_1(\text{TO})\), \(E_1(\text{TO})\), and high-frequency \(E_2^{\text{H}}\) phonons of GaN, respectively.

The obtained Raman spectra were fitted by three Lorentz functions originating from the \(A_1(\text{TO})\), \(E_1(\text{TO})\), and \(E_2^{\text{H}}\) phonons, but the fittings are not good between the \(A_1(\text{TO})\) and \(E_1(\text{TO})\) phonons. Then we obtained excellent fittings by assuming four Lorentz functions, as shown in Raman spectrum at \(\theta = 0\) of Fig. 1, indicating that there is a quasi-TO mode, i.e., an \(A_1(\text{TO})-E_1(\text{TO})\) mixing mode, because of the polariton effect [10]. There are ordinary and extraordinary polar modes in the uniaxial crystals, and the latter modes of TO or LO phonons are mixed, respectively, by the electromagnetic field when the anisotropic effect is weak. The peak of the quasi-TO phonon observed between the \(A_1(\text{TO})\) and \(E_1(\text{TO})\) phonons was very broad, reflecting the distribution of the propagation direction of the phonon polariton. Then it is difficult to distinguish not only the ordinary \(E_1(\text{TO})\) and quasi-TO modes but also pure \(A_1(\text{TO})\) and quasi-TO modes because of the \(A_1(\text{TO})-E_1(\text{TO})\) mixing. Moreover, the selection rule of the quasi-TO modes does not necessarily agree with that of the \(A_1(\text{TO})\) or \(E_1(\text{TO})\) mode. Since the microscope has a large solid angle, this effect is strong in the present experiment.

Recently, it was reported that the polarization dependence of the \(A_1(\text{TO})\) phonon could be expressed by the complex-valued Raman tensors in GaN [8, 11]. On the other hand, Hsiao et al. [9] stated that the Raman selection rules were determined by the real-valued Raman tensors in GaN nanorods and still follow those of bulk GaN. We think that the contradictory results are probably due to the effect of polariton.

It is not necessary to take the polariton effect into account for the \(E_2^{\text{H}}\) phonon, because it is not a polar mode. Hereafter, we focus our attention on the \(E_2^{\text{H}}\) phonon in order to study the size effect in the selection rule of Raman scattering of GaN nanocolumns.

Figure 2 shows the dependence of the Raman intensity of \(E_2^{\text{H}}\) phonon in single GaN nanocolumns with various diameters.

The integrated Raman intensity \(I\) of the two-fold degenerate \(E_2^{\text{H}}\) phonon in bulk crystal is given as

\[I = \sum_j |e_i \cdot R_j e_s|^2,\]

where \(R_j\) is the Raman tensor [10].

\[\begin{align*}
R^1(E_2^{\text{H}}) &= \begin{pmatrix} d & 0 & 0 \\ 0 & -d & 0 \\ 0 & 0 & 0 \end{pmatrix}, \\
R^2(E_2^{\text{H}}) &= \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.
\end{align*}\]

In the parallel-polarized case when both the polarizations \(e_i\) and \(e_s\) of incident and scattered lights are parallel to each other, i.e., \(e_i = e_s = (\sin \phi \sin \theta, \cos \phi \sin \theta, \cos \theta)\), where \(\phi\) is an angle from the \([1100]\) direction on the \(c\) plane, the Raman intensity \(I\) for bulk sample is given as

\[I(\theta) = d^2 \sin^4 \theta.\]

The intensity \(I(\theta)\) is independent of the angle \(\phi\), i.e., the side surfaces of hexagonal nanocolumn when the wave vector of the incident light is normal to the \(c\) axis. Even though the laser light is incident not only on the \((1100)\) plane but also on the \((10\bar{1}0)\) one in thin nanocolumns,

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the Raman intensity of the $E^H_2$ phonon depends on only the angle $\theta$. And it is not affected by the shape and size of the sample because the laser spot is always set at the center of the diameter of nanocolumns in this experiment. Equation (3) is denoted by a solid curve in Fig. 2. In the selection rule of bulk crystal, the $E^H_2$ phonon is forbidden in the $x(z,z)x$ polarization, i.e., $\theta = 0$, but it was observed, in particular the intensity of the $E^H_2$ phonon was almost independent of $\theta$ in the 0.45-μm sample. In the 2.1-μm sample, the weak appearance of the $E^H_2$ phonon in this polarization configuration is probably due to polarization leakage of optical alignment, indicating that the selection rule holds. Thus we observed a breakdown of the selection rule. One can see that the selection rule gets recovered with increasing diameter.

Figure 3 shows the $\varphi$ dependence of Raman spectrum in a single GaN nanocolumn with a 450-nm diameter. We change the polarization direction of the scattered light from $y$ crystal axis to $z(c)$ one when that of incident light is set to be parallel to the $y$ axis, i.e., we change the parallel polarization to the perpendicular polarization.

When the Raman intensity $I(\varphi)$ of the $E^H_2$ phonon in bulk sample is given as

$$I(\varphi) = d^2 \cos^2 \varphi.$$  \hfill (4)

The intensity $I(\varphi)$ is also independent of the angle $\phi_0$. Figure 4 show the $\varphi$ dependence of the Raman intensity of $E^H_2$ phonon in single GaN nanocolumns with various diameters. In the selection rule of bulk crystal, the $E^H_2$ phonon is forbidden in the $x(y,z)x$ polarization, i.e., $\varphi = \pi/2$, but it was observed. The selection rule gets recovered with increasing diameter as well as $I(\theta)$.

The present experiment clearly demonstrates that the polarization selection rule of Raman scattering from the $E^H_2$ phonon begins to be broken down in GaN nanocolumns possessing diameters thinner than 850 nm, which is approximately four times the wavelength of incident laser light inside the sample, taking into account that the refractive index is about 2.4 at 532 nm [12, 13]. In the parallel polarization, the Raman intensity of the $E^H_2$ phonon is almost independent of the angle $\theta$ between the polarization directions of incident (scattered) light and the long axis (the $c$ crystal axis) in the 0.45-μm sample, where the diameter is nearly twice the wavelength of incident laser light inside the sample. Similarly, the $\varphi$ dependence becomes weaker, i.e., the intensity in the perpendicular polarization approaches the parallel one with decreasing diameter of nanocolumns. These results indicate that the polarization characteristics of Raman spectra weaken with decreasing diameter of nanocolumn.

Yu et al. [14] studied polarized micro-Raman scattering in individual CuO nanorods with diameters of 20-120 nm and showed that the intensities of all Raman bands were essentially independent of the Raman tensors of bulk crystal but determined solely by the magnitude of the electric field component along the nanorod’s long axis. When the diameter of one-dimensional (1D) nanostructure is much less than the wavelength incident light, the electric field $E_i$ inside the 1D nanostructure is attenuated with respect to the external field $E_e$ for field component perpendicular to the long axis [6]:

$$E_i = \frac{2\varepsilon_0}{\varepsilon + \varepsilon_0} E_e,$$  \hfill (5)
where $\varepsilon(\varepsilon_0)$ is the dielectric constant of the 1D nanostructure (vacuum). On the other hand, the electric field inside is the same as that of incident field in the direction parallel to the 1D nanostructure. When $\varepsilon \gg \varepsilon_0$, the electric field perpendicular to the long axis is negligible and then the Raman intensities were determined by the electric field component parallel to the long axis. A similar result was observed in Raman spectra of single-wall carbon nanotubes [15]. Recently, Schäfer-Nolte et al. [5] studied Raman scattering in single GaN nanowires with diameters of 50-90 nm and found that the $A_1$(TO), $E_1$(TO), and $E_2^\text{H}$ phonons almost vanished when the nanowire was oriented perpendicular to the polarization of the incident light, although the selection rules allow them. The Raman intensities were determined by the electric field component parallel to the long axis. Raman spectra from these phonon modes were governed by the sized finite effect. However, our results that the depolarization characteristics of Raman spectrum becomes stronger with decreasing diameter of nanocolumns is not interpreted by this size effect, probably because the diameter of nanocolumn is larger than twice the wavelength of incident light inside the sample in the present experiment.

**IV. CONCLUSION**

We observed the breakdown of the polarization selection rule of Raman spectra from $E_2^\text{H}$ phonon in single GaN nanocolumns possessing 0.45-2.1 $\mu$m diameters. It occurs when the sample diameter is thinner than four times the wavelength of the incident light inside the sample. The depolarization of Raman spectra from Raman-active phonons becomes stronger with decreasing diameter of nanocolumns.

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