Raman Scattering in GaN Nanocolumns and GaN/AlN Multiple Quantum Disk Nanocolumns *

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I. INTRODUCTION

Recently, the semiconductor columnar nanostructures, i.e., nanocolumns, have aroused great attention because of their potential uses in both the mesoscopic research and the development of nanodevices. In particular, GaN and the related nitrides are highly attractive materials and have received much interest for applications as blue-light-emitting and laser diodes. Yoshizawa et al.[1, 2] first succeeded in growing GaN nanocolumns on (0001) Al₂O₃ by RF-MBE, by means of 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] The self-organization process was applied to the fabrication of a novel columnar nanostructure, GaN/AlGaN heterostructure nanocolumns with GaN multiple quantum disk (MQD), grown on (0001) Al₂O₃ substrates.[4] Recently Kikuchi et al.[5] reported a fabrication of GaN-nanocolumn-based InGaN/GaN MQD light-emitting diodes (LEDs) on n-type (111) Si substrates.

In this work, we study phonon mode behavior in GaN nanocolumns and GaN/AlN-MQD nanocolumns by means of Raman scattering. In GaN nanocolumns we study a Fröhlich mode in three samples with different column densities, and confirmed that Raman scattering is a useful method to characterize the nanocolumnar crystals. Moreover, we study lattice dynamics in GaN/AlN MQD nanocolumns.
II. EXPERIMENTAL

GaN nanocolumns were self-organized on (0001) c-plane Al$_2$O$_3$ and (111) Si substrates by RF-MBE method.[1, 2] The nanocolumns were grown at high density as the c axis was maintained perpendicular to the substrate surfaces. The SEM photographs of the three samples studied by Raman scattering are shown in Fig. 1. In sample EP909, the AIN dots are first formed on the (0001) clean surface of Al$_2$O$_3$ as initial nucleation islands at 815-825°C, and then the GaN nanocolumn were grown at 847-860°C. In samples EP966 and EP972 the GaN dots are first formed on the (111) plane of Si at 562°C and 529-543°C, respectively, and then the nanocolumns were grown 910°C and 872-894°C, respectively. The average column diameter ranges from 40 nm to 100 nm and the column height is about 1.3 µm. The density of the nanocolumns is about 10$^{10}$ columns/cm$^2$. In general, the column density decreases as the growth temperature is increased when the same kind of substrate is used.

GaN/AIN MQD nanocolumns are grown on the (0001) Al$_2$O$_3$ substrates through the same self-organization process.[4] A few hundred pairs of GaN/AIN multi-layer structure were fabricated on the GaN nanocolumns by controlling the thicknesses of the GaN and AIN quantum disks. The schematic structure of the GaN/AIN MQD nanocolumns is illustrated in Fig. 2.

The 514.5 nm line of Ar$^+$-ion laser was incident on the c plane of the sample and Raman spectra were recorded in quasibackscattering geometry at room temperature. The scattered light was dispersed by a Jobin-Yvon T64000 triple-grating monochromator equipped with a microscope and detected by a liquid-N$_2$-cooled charge-coupled-device (CCD) detector.
III. RESULTS AND DISCUSSION

A. GaN nanocolumns

Fig. 3 shows Raman spectra in three samples (EP909, EP972, and EP966) of GaN nanocolumns self-organized on Al$_2$O$_3$ and Si substrates. Raman spectra of the GaN continuous film grown by RF-MBE on Al$_2$O$_3$ and the substrate Al$_2$O$_3$ are also given for comparison. The GaN crystal with a wurtzite structure has Raman-active phonons of one $A_1$, one $E_1$ and two $E_2$-symmetry modes. Among them the Raman-active $E_2$ and $A_1$(LO) phonons are observed at 565 and 737 cm$^{-1}$, respectively, in bulk GaN film. They are allowed in backscattering geometry when the incident light is perpendicular to the c plane. In the GaN nanocolumns, other Raman-active $A_1$(TO) and $E_1$(TO) appear at 531 and 557 cm$^{-1}$ in addition to an enhancement of Raman intensity in the $E_2$ and $A_1$(LO) phonons. The former phonons are forbidden in the true backscattering geometry. The significant breakdown of the polarization selection rules and the enhancement of Raman intensity in the $E_2$ and $A_1$(LO) phonons may be attributed to deviation from the strict backscattering geometry and the multiple scattering process.[6]

In the GaN nanocolumns we observed a Fröhlich mode, which is a surface-related vibrational mode and denoted by a triangle in Fig. 3, too. Fig. 4 shows Raman spectra between 600 and 800 cm$^{-1}$. The frequency and the line width of the Fröhlich mode change drastically in three samples EP909, EP972, and EP966. It was pointed out in porous GaP, which can be regarded as a system of interpolated columnlike pores in GaP, that the frequency of the Fröhlich mode depends strongly on the relative concentration of GaP in the air.[7] Tiginyanu et al.[6] observed it in a sample of GaN columnar nanostructures, which was fabricated by electrochemical dissolution of bulk material. They estimated the average concentration $c_0$, taking into account a Gaussian distribution and using the effective dielectric constant.

There are an ordinary and two extraordinary phonon modes of optical phonon in a wurtzite crystal. The ordinary phonon is always transverse and has $E_1$ symmetry. The extraordinary phonons are mixed $A_1$ and $E_1$ quasi LO or TO modes. It is well known that the Raman intensity of the ordinary phonon is much weaker than that of the extraordinary phonon.[8] The Raman spectrum $I(\omega)$ from the excitations of extraordinary phonons in a uniaxial crystal is given as[6]

$$I(\omega) \propto \text{Im} \frac{-1}{\varepsilon_\parallel \cos^2 \theta + \varepsilon_\perp \sin^2 \theta},$$  

(1)
where $\theta$ is the angle between the wave vector of the excitation and the $c$-axis. For the relative concentration $c$ of GaN in the air, the effective dielectric function parallel to the $c$-axis is given as

$$\varepsilon_\parallel = (1 - c) \varepsilon_\text{air} + c \varepsilon_\parallel^{\text{GaN}}$$

and that perpendicular to the $c$-axis, in the two-dimensional Maxwell-Garnett approximation, is written as

$$\varepsilon_\perp = \frac{(1 + c)\varepsilon_\parallel^{\text{GaN}} + (1 - c)\varepsilon_\parallel^{\text{air}}}{(1 - c)\varepsilon_\perp^{\text{GaN}} + (1 + c)\varepsilon_\parallel^{\text{air}}}.$$  

Here the dielectric functions of bulk GaN are

$$\varepsilon_\parallel^{\text{GaN}} = \varepsilon_\infty \left\{ 1 + \frac{\omega_{\text{GaN}}^2}{\omega_{\text{GaN}}^2 - \omega^2 - i \Gamma_{\text{GaN}}} \right\}$$

and

$$\varepsilon_\perp^{\text{GaN}} = \varepsilon_\infty \left\{ 1 + \frac{\omega_{\text{GaN}}^2}{\omega_{\text{GaN}}^2 - \omega^2 - i \Gamma_{\text{GaN}}} \right\},$$

and the dielectric constant of the air $\varepsilon_\text{air}$ is given as 1. Using the high-frequency dielectric constant $\varepsilon_\infty = 5.35$, $\omega_{\text{GaN}} = 736$ cm$^{-1}$, $\omega_{\text{E}_{1}^{\text{GaN}}} = 531$ cm$^{-1}$, and the half-width $\Gamma_{\text{GaN}} \to 0$, we calculated the frequency of the Fröhlich mode when $\theta = 0$, as shown in Fig. 5. It decreases with decreasing $c$, but it is degenerate with $A_1$(LO) phonon at $c \sim 1$. For $\theta \neq 0$ Eq. (1) gives rise to two peaks between $\varepsilon_\parallel^{\text{GaN}}$ and $\varepsilon_\perp^{\text{GaN}}$. Here we can set $\theta = 0$, because we measured Raman scattering in nearly backscattering geometry and the obtained spectrum from the Fröhlich mode exhibits only one broad peak.

As seen in Fig. 4, the observed peak of the Fröhlich mode is very broad, which cannot be explained only by the half-width $\Gamma_{\text{GaN}}$. Then, taking into account the inhomogeneity of the column concentration, we fitted the observed spectra by using Eq. (1) and averaging over $c$ with a Gaussian distribution function of $\exp\left[-(c-c_0)^2/\sigma_c^2\right]$.[6] Here we assume $\Gamma_{\text{GaN}} = 7.8$ cm$^{-1}$. Fig. 4 shows that the calculated curves fit well the observed Raman spectra. The average concentrations $c_0$ obtained by Raman scattering are shown in Fig. 5 in addition to the dispersion parameters $2\sigma_c$. It should be noted that the concentration estimated directly by the peak frequency is a little higher than the average concentration $c_0$.

We also estimated $c_0$ and $\sigma_c$ from the surface SEM photographs of Fig. 1. The black-and-white degree of the pixel ranges from 0 to 125 in the SEM photographs. So as to reproduce the contrast images of nanocolumns in the SEM photographs we determine the threshold of contrast between the black and white. Then we estimated the average concentrations $c_0$ as 0.40±0.04 in sample EP966 and 0.75±0.03 in sample EP909 by counting the number of the pixels more whitish than the threshold in about 600×480 pixels of the SEM photograph. These values agree well with the Raman-scattering results, 0.40 in sample EP966 and 0.73 in sample EP909. In sample EP972, it is estimated as 0.75 ± 0.10, while the Raman-scattering result was 0.64. Since the black-and-white contrast of the SEM photograph of sample EP972 in Fig. 1(c) was not good, it was very difficult to estimate $c_0$ precisely. Then the ambiguity was large. Moreover, as seen in Fig. 1(a), many columns tilt. It is found that the columns at the front surface are a little thicker than those at the bottom near the substrate in the case of Si substrate. Then we probably overestimated $c_0$ from the surface SEM photograph in sample EP972. On the other hand, the distribution parameter $\sigma_c$ depends on the size of sampling area $S$. We drew a histogram and estimated $\sigma_c$ by obtaining $c_0$ in a few thousands sampling areas which are randomly picked from the SEM photographs. In general $\sigma_c$ is proportional to $S^{-1/2}$. When we use the sampling area with a size of $\sim \lambda/2 \times \lambda/2$, the $\sigma_c$ obtained from the histogram approximately agrees with the Raman-scattering result, where $\lambda (=514.5$ nm) is the wavelength of the incident laser. This suggests that the Raman scattering discerns the properties of the nanocolumns, $c_0$ and $\sigma_c$, in the area with a size of $\sim (\lambda/2)^2$, which are averaged in the incident-light spot with a diameter of $\sim 30$ $\mu$m.

B. GaN/AlN Multiple Quantum Disk nanocolumns

Fig. 6 shows Raman spectra in GaN/AlN MQD nanocolumns with various thicknesses of GaN and AlN quantum disks. However, the thickness of AlN quantum disk may be regarded as almost constant when compared with that of GaN quantum disk. When the GaN quantum disk is thin, three peaks are observed at 531, 597, and 645 cm$^{-1}$ in addition to the Raman-active $E_2$ phonon of bulk GaN. It is noted that the frequency of the 531-cm$^{-1}$ peak corresponds to $A_1$(TO) phonon of bulk GaN. The 597-
FIG. 6: Raman spectra of the GaN/AlN MQD nanocolumns grown on Al$_2$O$_3$. Raman spectra of the GaN/AlN superlattice film grown by RF-MBE and the substrate Al$_2$O$_3$ are also given for comparison. Peaks of the substrate Al$_2$O$_3$ are denoted by red letters of A.

and 645-cm$^{-1}$ peaks gradually disappear with increasing thickness of GaN quantum disk. On the other hand, two new peaks appear at about 548 and 579 cm$^{-1}$ and shift gradually to the low-frequency side with increasing thickness of GaN quantum disk. Simultaneously the intensity of the E$_2$ phonon of GaN drastically increases. In the 52.2/23.0-Å sample we observed three peaks at 485, 692, and 708 cm$^{-1}$. All of the new peaks were not observed in a usual GaN/AlN superlattice film grown by RF-MBE, which has fifty pairs of GaN/AlN.

Gleize et al.[10] calculated the dispersion of polar optical phonons along the layer direction in wurtzite GaN/AlN heterostructure superlattice in the framework of the dielectric continuum model. The extraordinary phonons are classified into three kinds of phonon modes; confined modes in either one of two layers, quasi-confined modes confined in one type of layer and evanescent in the other, and interface modes localized at the interfaces of two layers and decaying exponentially from the interfaces in both layer.

In the nanocolumns the wave vectors along the radial direction of column should be quantized. Although the result of Gleize et al. cannot be simply applied to the present experimental result, we try to assign the new peaks. The 548-cm$^{-1}$ peak, appearing between $\omega_{\text{GaN}}^{\text{AlN}}$ and $\omega_{\text{AlN}}^{\text{GaN}}$, is assigned to a quasi-confined mode existing strongly within the GaN layers.[10] The 645-cm$^{-1}$ peak comes from a quasi-confined mode in the AlN layers, because it is observed between $\omega_{\text{AlN}}^{\text{GaN}} = 614$ cm$^{-1}$ and $\omega_{\text{GaN}}^{\text{AlN}} = 673$ cm$^{-1}$ and the scattering efficiency is large when the GaN quantum disks are thin. Two new peaks at about 579 and 597 cm$^{-1}$ originate from interface modes, because they appear in the frequency region where $\varepsilon_{\perp}^{\text{GaN}}/\varepsilon_{\parallel}^{\text{GaN}} > 0$ and $\varepsilon_{\parallel}^{\text{GaN}}/\varepsilon_{\parallel}^{\text{AlN}} < 0$ are satisfied, i.e., between $\omega_{\text{E}_n^{\text{GaN}}} = 557$ cm$^{-1}$ and $\omega_{\text{E}_n^{\text{AlN}}} = 614$ cm$^{-1}$.

The 531-cm$^{-1}$ peak, whose frequency corresponds to A$_1$(TO) phonon of bulk GaN, is a quasi-confined mode in the MQD nanocolumns. The E$_2$ and A$_1$(LO) peaks are proper confined modes. Moreover, we observed three more peaks at 485, 692, and 708 cm$^{-1}$ in the 52.2/23.0-Å sample. The 692 and 708 cm$^{-1}$ may be assigned to the Fröhlich mode. It appears probably because the GaN disks are thick and the effects of the MQD structures are weakened. It splits into two peaks when the wave vector of the excitation is not parallel to the c-axis, i.e., $\theta \neq 0$ in Eq. (1). The calculated curve reproduces the present profile assuming the average concentration $c_0 = 0.44$, the dispersion parameter $\sigma_c = 0.06$, and $\theta = 0^\circ$. The 485-cm$^{-1}$ peak cannot be understood at present, because its frequency is lower than $\omega_{\text{E}_n^{\text{GaN}}}$. The quasi-confined and interface modes are not allowed in this region. Further theoretical studies in lattice dynamics of the columnar nanostructure are necessary to clarify the origin of this peak.

We could not observe confined, quasi-confined, and interface modes in the GaN/AlN superlattice film grown by RF-MBE, as shown in Fig. 6. Phonons with a wave vector of $q \sim 0$ are excited by Raman scattering. Then the frequencies of the quasi-confined modes at $q \sim 0$ in the GaN/AlN superlattice film are equal to the E$_1$(TO) phonons of bulk materials.[10] The quasi-confined modes at 548 and 645 cm$^{-1}$ are split from the GaN E$_1$(TO) and AlN E$_1$(TO) phonons, respectively; it is probably due to the quantization of the wave vector along the radial direction of nanocolumn. Moreover, the multiple scattering process enhances the scattering efficiency. The observed Raman peaks from the confined, quasi-confined, and interface modes are sharp. And the frequencies of the confined phonon modes hardly changed in the MQD nanocolumns when compared with the corresponding phonons of bulk GaN. These facts indicate the presence of heterointerfaces between two layers and suggest that the columnar nanostructures relieve strains at the barriers.

IV. CONCLUSION

By means of Raman scattering we studied a Fröhlich mode in three samples of GaN nanocolumns self-organized on Al$_2$O$_3$ and Si substrates. It was demonstrated that the Raman profile from the Fröhlich mode gives information about the column density and its inhomogeneity, which are measured with a size scale of the square of about a half wavelength of the incident laser light. Several confined, quasi-confined and interface modes were observed in the GaN/AlN MQD nanocolumns, while they were not observed in the usual GaN/AlN superlattice film. They
are activated probably because the wave vectors along the radial direction of disk are quantized by columnar nanostructures and the Raman intensities are enhanced by the multiple scattering process. The origin of the new peak at 485 cm\(^{-1}\) is not understood at present. Further theoretical and experimental studies are necessary to understand lattice dynamics of the semiconductor columnar nanostructures.

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