Fröhlich modes in GaN columnar nanostructures

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GaN columnar nanostructures fabricated by electrochemical dissolution of bulk material have been studied by micro-Raman spectroscopy. The anodization induces an increase in the intensity of Raman scattering accompanied by a breakdown of the polarization selection rules and by the appearance of a new mode at 716 cm$^{-1}$, i.e., in the frequency gap between the transverse optical and longitudinal optical bulk phonons. We present a Raman line-shape analysis based on the effective dielectric function of a composite that brings to light the Fröhlich character of this mode.

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GaN and related nitrides become recently the most intensively investigated semiconductor materials due to the progress achieved in epitaxial growth of layered structures such as high-quality GaN films on sapphire substrates using low-temperature GaN buffers, layered GaN/AlN and GaN/AlGaN heterostructures suitable for band gap engineering in the spectral range 3.4–6.2 eV, etc. The progress in layer-growth technology opens perspectives for numerous applications such as the creation of full-color display systems, data storage devices, solar-blind ultraviolet detectors, new sensor technologies, wireless communications, solid-state lighting and high-power microwave generation for radar, etc. Note that nitride-based light-emitting diodes and lasers have been successfully commercialized. Unique possibilities to further extend the areas of practical applications of nitrides may be provided by material nanostructuring. In particular, nanotexturization is expected to induce a strongly enhanced nonlinear optical response that may lead to the development of fully integrated light source and frequency converter subsystems.

Nanostructuring provides also important degrees of freedom for phonon engineering. It may change considerably the density of phonon states, induce surface-related vibrations, and spatially confine the bulk phonon modes. In GaP and InP films subjected to nanotexturization via electrochemical etching, Fröhlich-type vibrations have been recently observed in spontaneous Raman scattering (RS) and infrared reflection spectra. The frequencies of the Fröhlich modes can be tuned within the frequency gap between bulk TO and LO phonons which is expected to have a significant impact on the development of novel phonon-assisted electronic devices. In this work, we present the results of a micro-Raman scattering study of GaN columnar nanostructures obtained by illumination-assisted anodic etching of bulk layers. The observation of Fröhlich-type modes in nanostructured GaN is reported.

The GaN layers used in our experiments were grown by low-pressure metalorganic chemical-vapor deposition (MOCVD) on (0001) c-plane sapphire using a modified EMCORE GS-3200 system and trimethylgallium (TMGa) and ammonia (NH$_3$) as source materials. A buffer layer of about 25-nm-thick GaN was first grown at 510°C. Subsequently a 0.5-μm-thick n-GaN followed by a Si-doped n$^+$-GaN film and a top n-GaN layer with 2.0 μm thickness each were grown at the temperature 1100°C. For the purpose of comparison, samples without intermediate 0.5-μm-thick n-GaN and 2-μm-thick n$^+$-GaN films were fabricated as well. The concentration of free electrons in the top n-GaN layer was 1.7×10$^{17}$ cm$^{-3}$. Anodic etching of samples containing intermediate 0.5-μm-thick n-GaN and 2-μm-thick Si-doped n$^+$-GaN films was carried out at current density 5 mA/cm$^2$ in 0.1 mol aqueous solution of KOH under in situ UV illumination provided by focusing the radiation of a 250 W Hg lamp on the GaN surface exposed to electrolyte. The duration of the anodization was 6 min, leading to a top GaN columnar structure with the thickness of about 1.5 μm. A scanning electron microscope (SEM) image taken from such a structure is illustrated in Fig. 1(a). GaN columns with transverse dimensions of 50 nm or less prove to be oriented perpendicular to the initial surface. To estimate the density of dislocations in the top n-GaN layer, we used the photovoltaic etching (PEC) etching technique proposed by Youtsey et al. The absence of external electrical bias between the sample and Pt electrode resulted in a selective etching away of the material between threading dislocations [see Fig. 1(b), where whiskers are related to dislocations]. A comparison of SEM images presented in Fig. 1 shows that the density of columnar nanostructures obtained by anodic dissolution of the top n-GaN layer is much higher than the density of threading dislocations in the as-grown material.

The micro-Raman spectra were excited with the 488-nm...
line of an Ar$^+$ laser at room temperature. The laser beam was focused into a spot of about 2 $\mu$m on the sample. To avoid heating effects, the laser beam power was reduced to 2 mW. The scattered light was analyzed in a nearly back-scattering geometry by a triple Jobin Yvon T64000 monochromator with a spectral resolution $0.5$ cm$^{-1}$.

Figure 2 illustrates the micro-Raman spectra of columnar GaN as well as of bulk GaN and of the sapphire substrate for comparison. The spectrum of as-grown GaN taken from a sample containing no intermediate Si-doped n$^+$-GaN film exhibits strong scattering at the $E_2$ and $A_1$(LO) modes allowed in backscattering geometry. At the same time weak features related to forbidden $A_1$(TO) and $E_1$(TO) modes are observed which may be attributed to crystal lattice disorder and to deviation from the true backscattering geometry. The peaks seen on both curves marked by crosses are caused by light scattering in the sapphire substrate, the exciting light with quantum energy much lower than the band gap energy of GaN penetrates into the substrate, inducing a pronounced contribution to the RS spectrum.

The RS spectrum taken from the columnar GaN shows practically no contribution from sapphire. It exhibits strongly enhanced RS accompanied by a significant breakdown of the polarization selection rules. The two transverse $A_1$(TO) and $E_1$(TO) modes from the poles of the bulk dielectric functions

$$
\varepsilon_{A_1}^{GaN} = \varepsilon_{E_1} = \varepsilon_\infty \left[ 1 + \frac{\omega_{A_1}^2}{\omega_{A_1}^2 - \omega^2 - i \omega \gamma} - \frac{\omega_{pl}^2}{\omega^2 + i \omega \Gamma} \right]$$

and

$$
\varepsilon_{E_1}^{GaN} = \varepsilon_{E_1} = \varepsilon_\infty \left[ 1 + \frac{\omega_{E_1}^2}{\omega_{E_1}^2 - \omega^2 - i \omega \gamma} - \frac{\omega_{pl}^2}{\omega^2 + i \omega \Gamma} \right]
$$

($\varepsilon_\infty = 5.35$, $\omega_{A_1} = 735$ cm$^{-1}$, $\omega_{A_1}(TO) = 533$ cm$^{-1}$, $\omega_{E_1}(LO) = 742$ cm$^{-1}$, and $\omega_{E_1}(TO) = 561$ cm$^{-1}$, respectively, are forbidden in strict backscattering geometry. Like in porous GaP$^5$ the breakdown of the selection rules may be attributed to strong diffuse scattering of the laser beam inside the columnar GaN layer. In fact, the absence of RS contributions from sapphire is indicative of effective light ‘‘trapping’’ in the GaN columnar structure. The multiple scattering of light in the top columnar layer seems to be the reason for the increase in the RS intensity by more than one order of magnitude. An entirely new feature in the spectrum of columnar GaN in comparison with bulk GaN is the broad shoulder on the left-hand side of the RS band related to the $A_1$(LO) mode (Fig. 3). This new RS peak can be interpreted as caused by Fröhlich modes. According to the SEM image [Fig. 1(a)], the upper part of the sample can be described by GaN columns in an air matrix with the corresponding large enhancement of anisotropy. The effective dielectric function then is given by
FIG. 3. Experimental (solid line) and theoretical (dash-dotted line) Raman spectra of columnar GaN. The theoretical curve caused by Fröhlich modes only (dashed line) is obtained with the parameters $\sigma=5^\circ$, $\sigma_r=0.20$, and $c_0=0.57$. The fit to the peak at $\omega=740$ cm$^{-1}$ (dotted line), the $\omega_{A_1(LO)}$ peak slightly shifted in frequency by its interaction with plasmons, corresponds to $\gamma=8.5$ cm$^{-1}$, $n=1.75\times10^{17}$ cm$^{-3}$, $\mu=400$ cm$^2$/V s, and $m^*=0.21$ ($\omega_p=118$ cm$^{-1}$ and $\Gamma=111$ cm$^{-1}$).

\[ \varepsilon_{\parallel}=(1-c)\varepsilon_{\text{air}}+c\varepsilon_{\text{GaN}} \]  
(exactly) and

\[ \varepsilon_{\perp}=(1+c)\varepsilon_{\text{GaN}}+(1-c)\varepsilon_{\text{air}} \]  
(in a two-dimensional Maxwell-Garnett approximation),

where $c$ is the relative concentration of GaN and $\varepsilon_{\text{air}}=1$. Single columns ($c\rightarrow0$) would result in a Fröhlich mode given by $\varepsilon_{\perp}^{\text{GaN}}+\varepsilon_{\perp}^{\text{air}}=0$ at $\omega=716$ cm$^{-1}$, just in the region of the broad shoulder in Fig. 3. The Raman intensities due to the excitation of ordinary and extraordinary phonons are

\[ I_o \sim \text{Im} \varepsilon_{\parallel} \text{ and } I_{eo} \sim \text{Im} \left[ (\omega/\varepsilon_{\parallel}\cos^2\theta+\varepsilon_{\perp}\sin^2\theta) \right], \]

where $\theta$ is the angle between the exciting light wave vector $k$ and the column direction parallel to the $c$ axis. The $I_{eo}$ scattering is much smaller than the scattering by TO phonons $\text{Im} \varepsilon_{\parallel}$ and can be neglected compared with the $I_{eo}$ scattering using the Faust-Henry coefficient given by Kozawa et al.$^{11}$ $I_{eo}$ gives rise to two peaks on the left-hand side of $\omega_{A_1(LO)}$, but their half-widths are too small in comparison with the experimental data. We therefore took into account multiple scattering by averaging $I_{eo}$ over $\theta$ with a weight $\sim \exp(-\theta^2/\sigma^2)$. Additionally we took into account the inhomogeneity of the sample by averaging over $c$ with a weight $\sim \exp(-c-c_0)^2/\sigma_c^2$. The best fit obtained in this way is shown in Fig. 3 by the dashed curve which is in reasonable agreement with the experimental spectrum. We remark that the broad shoulder below $\omega_{A_1(LO)}$ is essentially due to the upper peak in $I_{eo}$; the intensity of the lower one nearly vanishes.

In conclusion, GaN columnar nanostructures fabricated by anodic etching of bulk GaN layers show enhanced Raman scattering and breakdown of the polarization selection rules. An RS band at frequency 716 cm$^{-1}$ was evidenced in columnar GaN and attributed to Fröhlich vibrational modes. This interpretation was confirmed by the Raman line-shape analysis based on the effective dielectric function of a composite.

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