One-dimensional semiconductor nanowires of the wide band gap semiconductor gallium nitride (GaN) are prime candidates for future nanoscale devices such as short wavelength optoelectronic devices, high-power/temperature electronics, or sensors for biological applications.1–3 The electrical and optical properties of nanowires depend heavily on their crystalline structure and composition.1,4 Subsequently, it is important to measure their homogeneity and composition at the level of single wires and to correlate these with the nanowire dimensions and optical properties.5 In this context, optical microscopy and spectroscopy are able to provide information that goes far beyond visualizing the physical shape of materials. As demonstrated for the study of single carbon nanotubes,6,7 Raman scattering is very helpful to probe the mechanical stress, thermal history, phonon confinement, and lattice dynamics, correlating optical spectra with the nanowire’s crystallographic anisotropy and geometry. Raman confocal microscopy has a spatial resolution of roughly half the excitation wavelength, thus far limiting its use for the characterization of aggregated bundles of nanowires, and, as far as we know, far-field characterization of an individual nanowire together with polarization analyses has not yet been reported.8,9

In the present work, polarized Raman measurements were conducted locally with a confocal microscope (Horiba Jobin-Yvon Labram HR800) in conjunction with a high-resolution piezoelectric stage (PI) for accurate and reproducible positioning in order to characterize GaN nanowires that have their c axis either along or perpendicular to their growth direction. Different sets of polarization input and output were used to assign unambiguously the phonon modes of the crystalline structures. Raman spectra under the polarization configurations YZZY, YXXY, and YXYX are shown in Figure 1. The excitation wavelength was fixed at λ = 514.5 nm, and the input/output polarizations were selected with a half-waveplate and a polarizer, respectively. The nanowire has a diameter of 170 nm and was aligned so that the Z polarization direction matches the growth direction (i.e., the c axis for the ⟨001⟩ orientation) of the nanowire.

As reported by various authors for thin films10,11 and for collections of nanowires,9,12 GaN that crystallizes in the hexagonal wurtzite-type structure belongs to the space group C6v and has two formula units per primitive cell. According to the factor group analysis, the Raman active modes are 1A1 + 1E1 + 2E2, while 2B1 modes are silent. Since the wurtzite structure is noncentrosymmetric, both A1 and E1 modes split into longitudinal optical (LO) and transverse optical (TO) components. For a single GaN nanowire, four main signals are observed in Figure 1 at 142, 530, 558, and 568 cm⁻¹, and they can be assigned to E2(high), A1(TO), E1(TO), and E2(high) symmetry type modes, respectively. In the Y(ZZ)Y configuration, only the E1(TO) mode is observed, and the peak at 530 cm⁻¹ (A1(TO)) denotes a polarization leak. The broad peak mode at 660 cm⁻¹ is assigned to a defect state with an energy close to the A1(LO) or to the first overtone of a B1 silent mode. This demonstrates that confocal techniques may be used as an easy, inexpensive, and rapid way to characterize the phase and growth direction of single nanowires.

Mapping of the nanowire was performed by recording step-spectra every 200 nm with an integration time of 1 s. A 100X NA = 0.9 microscope objective was used. Furthermore, no spectral shifts were observed with longer collection times, suggesting that possible laser heating is not affecting the crystal lattice. By intensity integration of the [509–552 cm⁻¹] spectral domain around the A1(TO) mode (530 cm⁻¹), the variations of the Raman signal over the full nanowire are investigated (Figure 2). The images show details with lateral resolution better than 200 nm and with a reasonable acquisition time of about 1 h for a complete polarized image. For the Y(ZZ)Y polarization configuration, Figure 2a shows that the signal is maximum on the straight portions of the nanowire, while it disappears on the bent portion of the nanowire. The complementary image (Figure 2b) is obtained by integration of the E2(high) mode at 568 cm⁻¹. In the Y(XX)Y polarization configuration, the opposite spectroscopic contrast is observed with a maximum signal of the 568 cm⁻¹ mode in the straight portions of the wire as observed in Figure 2c and a maximum signal for the A1 mode in the horizontal part of the nanowire. Under these scattering configurations, the optical longitudinal phonon modes were not observed.

To complement these polarized spectra, we have also measured nonpolarized spectra of an isolated, horizontal GaN nanowire grown in the [110] direction with its c axis oriented perpendicular to that of growth. Due to cylindrical geometry of this nanowire, the angular position of c relative to the substrate plane is not known (Figure
3b). For $Y(XX+XZ)\bar{Y}$ spectra (Figure 3c), the input polarization is along the growth direction, and no analyzer was used. Only the two $E_2$ modes (low and high) can be observed at 143 and 568 cm$^{-1}$, respectively. With an orthogonal polarization input relative to the growth direction, $Y(ZZ+ZX)\bar{Y}$, only $E_1$ and $E_2$(high) at 559 and 568 cm$^{-1}$, respectively, can be observed. It is noteworthy that the $A_1$(TO) mode is not clearly defined, and only a broad background signal of nanomaterials with spectral-map features smaller than 200 nm. Furthermore, polarization measurements demonstrate the ability to gain information on the nanowire’s phase, growth direction, and radial crystallographic orientation. In the future, the use of a high-resolution spectrometer should enable observation of stress-induced shifts and crystallinity modifications at various growing temperatures for individual nanostructures.

In summary, we have performed a complete polarized Raman study of single GaN nanowires using a confocal microscope together with a high-resolution stage. The Raman assignments compare well to those from thin films, and studies on epitaxially grown nanowires show mainly first-order Raman effects. The high spatial resolution of the Raman confocal instrument together with a piezoelectric stage demonstrates unambiguously the possibility to image the Raman signal of nanomaterials with spectral-map features smaller than 200 nm. Furthermore, polarization measurements demonstrate the ability to gain information on the nanowire’s phase, growth direction, and radial crystallographic orientation. In the future, the use of a high-resolution spectrometer should enable observation of stress-induced shifts and crystallinity modifications at various growing temperatures for individual nanostructures.

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**Supporting Information Available:** Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

References


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