

Crystallographic Characterization of GaN Nanowires by Raman Spectral Image Mapping

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August 12, 2009

Abstract

Obtaining structural information of nano-structured materials often requires electron microscopy for sufficient spatial and crystallographic resolution. This study uses Raman spectral imaging to extract information regarding crystalline orientation and structure by non-invasive means. Seeking a correlation between crystallographic facet and favored Raman mode, Gallium Nitride (GaN) nanowires were imaged by confocal Raman microscopy with a 532nm laser, and scanning electron microscopy. Raman spectral maps containing pixel-by-pixel spectra were acquired. Comparison to scanning electron microscope (SEM) images revealed that for regularly-shaped wires at least 230nm in width, the E_2 mode is observed more strongly in the $[1\ 1\ 2]$ and $[-1\ -1\ 2]$ “smooth” facets of the wire, while the $A_1(\text{TO})$ mode is only observed in the $[0\ 0\ 1]$ “rough” facet, suggesting a strong surface-structure dependence of Raman signal that can be exploited for imaging. Further experimentation on irregular and small wires that exhibit only the E_2 peak, on other favored modes in GaN, and with other group III/V nitrides is recommended.

In recent years, increased difficulty in improving the performance of silicon-based electronic integrated circuits, an alarming need for alternative forms of energy conversion and storage, and a desire to design efficient lighting mechanisms have contributed to an expansion of research and investment in fields that would complement, or even come to replace currently-existing technologies. One such field that has garnered particular attention is optoelectronics, the study of electronic devices that allow the control and directed use of light. An interface with nanotechnology would further the development of efficient, novel devices such as photodiodes (for use in photovoltaics) and even integrated optical circuits which rely on photon rather than electron transport.

Materials considerations and investigations have spawned interest in highly crystalline nitrides of group III and V elements, especially Gallium Nitride (GaN), for short-wavelength (blue and UV) devices. These materials demonstrate robustness against heat, high voltage, and ionizing radiation. Their anisotropic geometry and polar nature contributes to these unique qualities [4]. A large bandgap (3.45eV for GaN [3]) also allows these nitrides to operate at higher temperatures than current transistors. Also, a material that is used as an optical interconnect must operate without reflection losses of light, which a high index of refraction can cause. As a result, another property of particular importance is

that a nanoscale interface allows the nitrides to exhibit lower effective indices of refraction than their bulk counterparts. Continued efforts are being made today in fully characterizing these materials, and designing methods for optimizing and taking advantage of their useful properties. [2]

Two important considerations in researching the properties of nanostructures for optical uses are a material’s vibrational and dielectric properties, as these determine how a material behaves as an optical waveguide. Only specific vibrational transitions are allowed within a given molecule due to its structure and chemical makeup; these must be determined, along with the effect of their interaction.

Raman spectroscopy can be used to experimentally determine a specific structure’s vibrational and dielectric properties. By sending incident photons with a controlled frequency via laser at the molecule in question, scattered photons are captured and analyzed. The buildup of photons with a frequency offset ($\pm\nu$), usually measured in relative wavenumbers, from the original laser’s frequency, make up the Stokes/anti-Stokes (Raman) bands of the emitted spectrum. This frequency offset determines the change in energy of the molecule after losing or gaining energy as a result of the interaction with the photon. Figure 1 depicts all possible changes in energy that a molecule can go through after interacting with a photon. Most molecules begin at the ground state,

are excited by a photon from the laser into a virtual state, and fall back down into an excited vibrational state. These photons, scattered at a lower energy than the fundamental laser, are called Stokes scatter. Photons that are scattered elastically, the vast majority of scattered photons, are Rayleigh scattered. A small percentage of molecules begin in an excited vibrational state, get raised to a virtual state, and fall back down to the ground state. This causes the scattering of a photon with less energy than the original. These are called anti-Stokes photons. This study focuses on Stokes scattering. Fundamentally, Stokes and anti-Stokes bands are identical energetically and are only different in scattering intensity. The sensitive nature of molecular vibrations makes it such that Raman modes are highly molecule-specific. In other words, different molecules cause very distinct Raman shifts, both in the frequency offset and in the intensity. A simple spectrum allows one to deduce the chemical makeup of a sample.

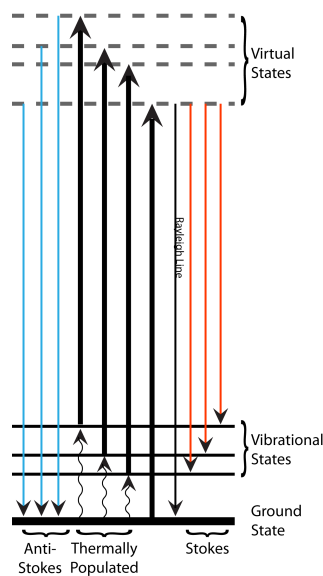


Figure 1: Energy Level representation of Raman shifts

Previous studies on the Raman behavior of GaN have explored various topics including angle-dependent Raman scattering [1] and the effect of anisotropic strain on Raman modes [5]. The angle-dependence study concluded that peak intensity depends sinusoidally on the angle between laser polarization and the length of the rod. The anisotropic strain study demonstrated a link between strain and the splitting of $E_1(\text{TO})$, $E_1(\text{LO})$ and E_2 peaks, and the frequency location of the $A_1(\text{TO})$ peak.

With this tool available, the answer to another important question can be sought: can we observe differences in structure in sub-wavelength sized structures by optical means? In other words, what is the relation between facet and mode? The wires in question are composed of diagonally-oriented planes of GaN molecules stacked together to form a triangular prism, as depicted in Figure 2. Two chemically identical facets, $[1\ 1\ 2]$ and $[-1\ -1\ 2]$, terminate the GaN planes and are considered the “smooth” faces of the wire, while a third facet, $[0\ 0\ 1]$ is the surface of a single GaN plane, and is considered the “rough” face of the wire. Often, the “rough” side is observed where GaN planes do not extend across the entire length of the wire, leaving a staircase-like structure made up of individual lattice planes.

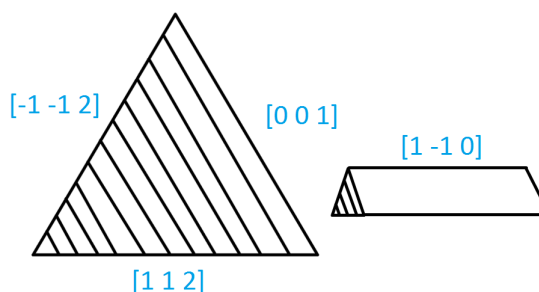


Figure 2: Schematic representation of facets in a GaN wire

When incident laser light of a specific polarization interacts with a wire, the orientation of molecules, or crystalline lattice, at the spot of incidence affects which phonon modes are favored and more heavily-induced. Consequently, the intensity of different Raman peaks observed varies according to the physical structure of the focal spot. If a correlation can be observed experimentally between the incident crystallographic facets on GaN nanowires and observed modes at specific points on the wire, important physical information can be extracted from simple Raman spectroscopy, rather than the more restricting and damaging SEM. Additionally, the limitations of Raman imaging due to resolution can be understood.

GaN wire samples grown via metalorganic chemical vapor deposition (MOCVD) were placed onto pre-scored glass coverslips. These score marks were used for indexing the individual wires in order to correlate Raman and scanning electron microscopy (SEM) measurements. The wires were first measured with a diffraction limited confocal optical microscope (WiTec alpha300 s) capable of Raman imag-

ing, equipped with a 100x, 1.4NA oil immersion objective lens (Olympus UPLSAPO 100XO) and 532nm fiber-coupled diode pumped laser. Individual wires were located optically, then scanned at about 200 nm/point, taking a full Raman spectrum at each point (with an integration time of 0.1 seconds). These spectra were filtered by energy to produce a “Raman map” depicting the spacial location of specific Raman modes. An example of a spectrum showing the two main peaks observed in this study, (A_1 (TO) and E_2), is shown in Figure 3, and an example of a Raman map depicting the intensity of the E_2 peak is shown in Figure 4.

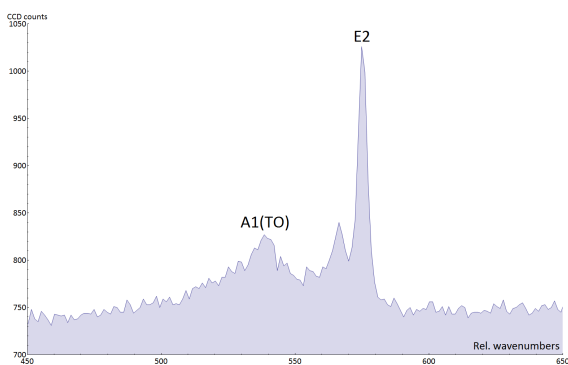


Figure 3: Example Raman spectrum for GaN wires taken using the setup described above. Both major raman peaks, A_1 (TO) and E_2 , are clearly visible.

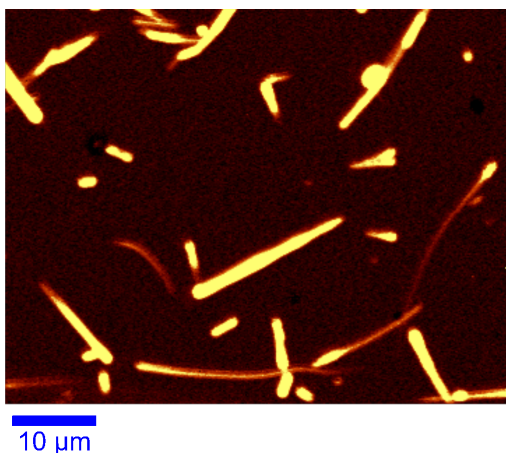


Figure 4: Spectral map of the E_2 mode over an area containing several wires

After scanning, the oil was cleaned off and the sample was placed under SEM (Zeiss Ultra 55), in order to achieve a high-resolution depiction of the

physical properties of each wire. With this, the two crystallographic facets can be identified by determining which side is the “rough” facet, either by locating the staircase-like structure mentioned previously, or by locating areas with wavy nature. The image can then be compared to the Raman map for the two modes to determine if there is a correlation between facet and favored mode. Initially, the immersion oil used with the 1.4NA objective lens had seeped through the scored glass slip on which the samples lay, rendering SEM imaging impossible. In order to resolve this, a 0.95NA air objective lens was used instead. However, this yielded poor images with no distinct A_1 (TO) mode. The original 1.4NA lens was again used, with caution towards the oil, and both the Raman and SEM imaging stages were successful.

Looking at the equation for resolution of a diffraction-limited system (R) in terms of wavelength (λ) and numerical aperture (NA): $R = \frac{1.22 * \lambda}{2 * NA}$, it is understandable why the 0.95NA objective lens performed poorly compared to the 1.4NA objective lens. With a 532nm laser wavelength, 0.95NA nets a resolution of 342 nm, while 1.4NA nets a resolution of 232 nm. A significant percentage of wires imaged had facet widths between these two values, rendering the 0.95NA objective useless in these diffraction-limited cases. Of course, there exist wires with facets less wide than the resolution for a 1.4NA lens, which poses a problem for properly imaging every wire present in a given sample.

Figure 5 shows the overlaid Raman maps for both peaks on a single wire. Green represents the intensity of the A_1 (TO) mode and red represents the E_2 mode. Yellow shows the overlap of the two. There is a clear delineation of the two bands, where the E_2 mode extends over the whole wire, while the A_1 (TO) mode is only visible on one face of the wire. Figure 6 is an SEM image of the same wire. The individual lattice planes are clear (circled area) on the wire and show that this is the “rough” facet. Wires that showed clean Raman spectra with two distinct peaks all favored the E_2 mode on the $[1\ 1\ 2]$ and $[-1\ -1\ 2]$ “smooth” facets, and the A_1 (TO) mode on the $[0\ 0\ 1]$ “rough” facet. Moving across the wire from one facet to the other, the intensity of one peak decreases while the intensity of the other peak increases, as seen in Figure 7. This continues along the length of the wire. At the ends of the wire intense peaks are observed due to significant waveguiding of the fundamental laser line within the wire. This causes intense Raman of both modes to emit from the end facets.

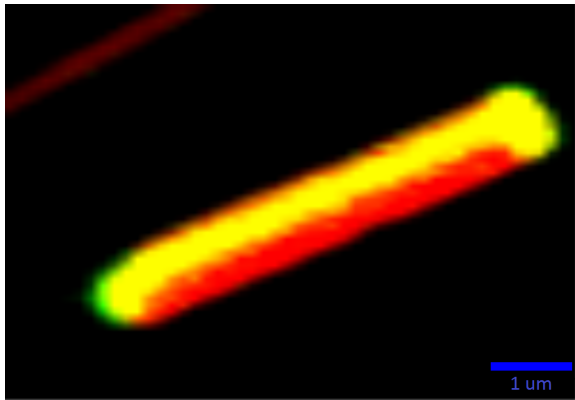


Figure 5: Overlaid spectral maps that depict the intensity of the two Raman peaks in question. The yellow region favors the $A_1(TO)$, while the red region favors the E_2 . Note the clear separation.

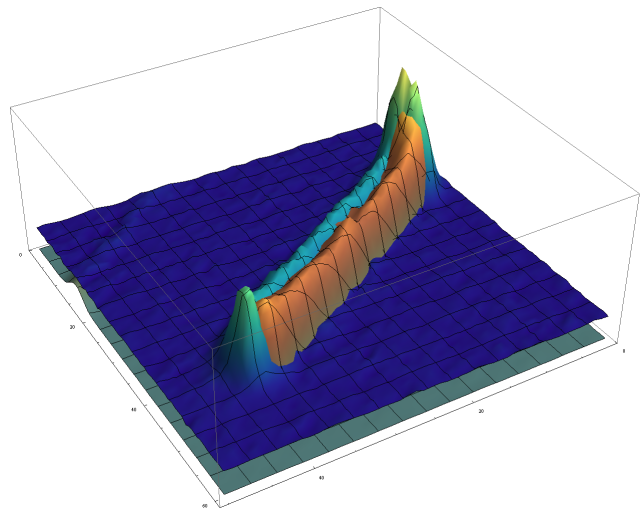


Figure 7: Intensity representation of the two Raman peaks across a 2D area. The orange surface represents E_2 , while the blue-green surface represents $A_1(TO)$. The plots are normalized, and the blue-green surfaced has been raised slightly for visibility.

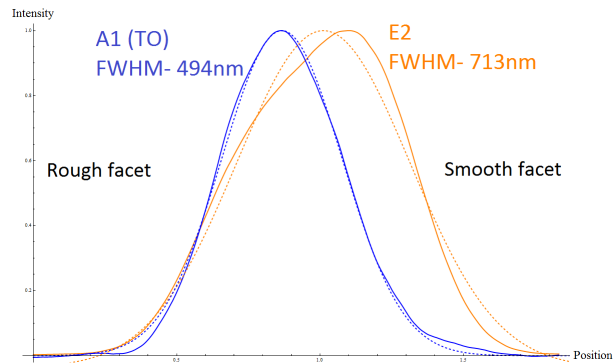


Figure 8: Cross section taken from a Raman map of the above wire. The spacial-dependent intensity of both bands are fitted to Gaussians, shown with dotted lines, and the full width at half-maximum of each fit is given.

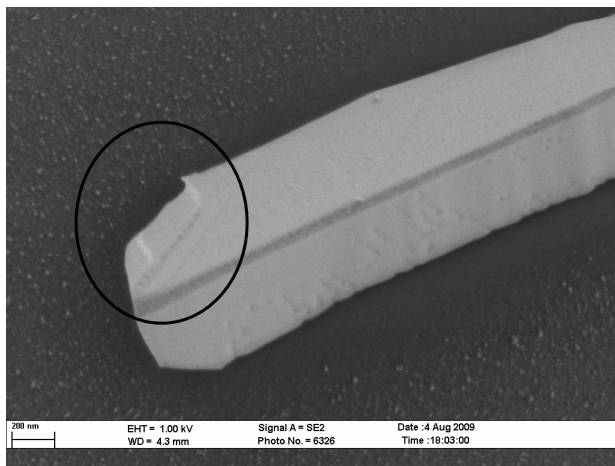


Figure 6: SEM image of the above GaN wire. The planar fragments that are circled give away the location of the “rough” $[0\ 0\ 1]$ facet.

Figure 8 shows a cross section of the spectral map taken along the wire shown in figure 7, with the intensity of each mode along the width of the wire fitted to a gaussian. From this it becomes clear that the E_2 mode has intensity on both facets, but is favored on the “smooth” facet, while the $A_1(TO)$ mode dies off quickly over the “smooth” facet. The SEM had previously revealed a “rough” side width of 448nm, and a “smooth” side width of 372nm. The rough side is wider than the smooth side, yet the mode that

is favored on the “rough” side, $A_1(\text{TO})$, is narrower than the mode that is favored on the “smooth” side, E_2 (494nm versus 713nm). This trend holds through every wire imaged, confirming a higher degree of localization of the $A_1(\text{TO})$ mode to the “rough” facet. It is clear that the E_2 mode cross-section does not fit well to a single gaussian and is likely bimodal, one gaussian for each facet of the wire. The E_2 mode is present on both sides of the wire, but there appears to be a distinct intensity peak for each facet. Also, it should be noted that every width mentioned is greater than the previously-calculated resolution of 232 nm.

It is important to note that the setup used in this experiment imaged through the wire, from the bottom. The interior of the wire, however, is uniform regardless of the geometry of the surface above. As such, these drastic differences observed when moving from one facet to another suggest that the surface of a material plays a significant role in the Raman spectrum that is observed.

Now that a method has been devised for obtaining information about the physical properties of GaN wires without use of SEM or transmission electron microscopy (TEM), it is important to consider the limitations. Even with the 1.4NA objective lens, many wires sampled did not exhibit a sufficiently intense $A_1(\text{TO})$ peak, making distinguishing a peak from the spectrum noise increasingly difficult. This could be attributed to small wire size, irregular wire shape and damaged wires. Tapering wires also exhibited this behavior at their narrow ends once the width dipped under the previously-calculated resolution of 232 nm. Figure 9 shows exactly this phenomenon, with the detected $A_1(\text{TO})$ peak shown in yellow disappearing once the wire becomes about 230nm wide. Also, a significant percentage of wires observed under SEM were inverted and at arbitrary angles off the substrate, such as that in Figure 10, with a single facet facing upwards, allowing for only one of the two major Raman peaks to show during spectroscopy.

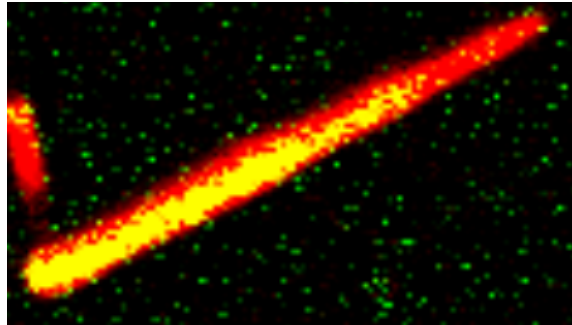


Figure 9: As the wire tapers, the $A_1(\text{TO})$ peak becomes less pronounced until it completely disappears at a wire width of 230nm.

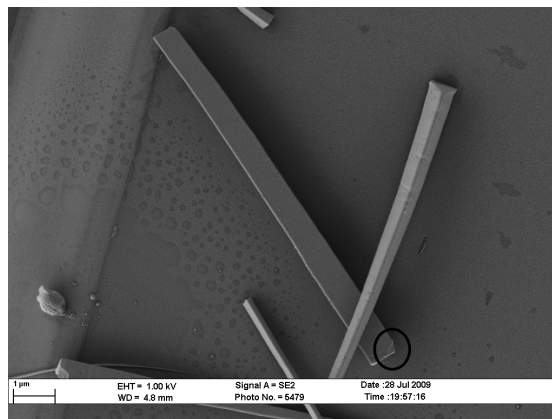


Figure 10: SEM image of an inverted nanowire with the “rough” $[0\ 0\ 1]$ facet facing upwards.

For future studies, this relation between observed Raman modes and crystallographic facets can be expanded further than the E_2 and $A_1(\text{TO})$ modes on GaN nanowires. Other than the previously-discussed E_2 and $A_1(\text{TO})$ modes, GaN nanowires also exhibit $E_1(\text{TO})$ and $E_1(\text{LO})$ modes, the latter of which would require a method to stand the wires up on their small triangular facets. Group III/V nitrides other than GaN can be tested.

This study has shown that it is possible to discern crystallographic orientation with non-invasive optical techniques, due to the heavily surface structure-dependent nature of the Raman modes. We have determined a lower limit of detectable resolution with our current system near the diffraction limit. Wires with a width over 230 nm can successfully and dependably be characterized and distinct crystallographic faces can be identified.

References

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