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418 cm$^{-1}$ Raman scattering from gallium nitride nanowires: Is it a vibration mode of N-rich Ga–N bond configuration?

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A Raman-active vibration mode at 418 cm$^{-1}$ is observed in wurtzite gallium nitride (GaN) nanowires synthesized by different growth methods. In particular, Raman scattering measurements of a number of GaN nanowires systematically prepared by nitriding $\beta$-Ga$_2$O$_3$ nanowires at different temperatures show an interesting evolution of the mode, revealing that it is most likely the vibration mode of N-rich octahedral Ga–N$_6$ bonds. This idea is further supported by the high-resolution transmission electron microscopic observation.

In addition to the characteristic Raman peaks at 564 and 720 cm$^{-1}$ of wurtzite GaN, one peak at 418 cm$^{-1}$ can be well seen in both the spectra. Besides this peak, another additional peak at 252 cm$^{-1}$ is observed. Other peaks marked by asterisk are from the Si substrate. It is more interesting to note that spectrum (b) in Fig. 1 exactly resembles the Raman spectrum of the GaN hollow spheres obtained by Sun and Li. These consistent observations of the 418 cm$^{-1}$ peak in the GaN nanostructures and in the strongly defected films prepared by different groups with a variety of techniques suggest that the Raman structure is likely to be a characteristic vibration mode of some unknown Ga–N bond configuration which exists abundantly in various forms of nano- and defected GaN structures.

In the past decade, the GaN-based optoelectronic industry has grown rapidly. More recently, various forms of GaN nanomaterials such as nanorods and nanowires have attracted a great deal of attention as these nanosized GaN materials are expected to exhibit superior optical and electrical properties that may greatly extend applications of GaN-based materials. For example, GaN nanorods and nanowires have been used to fabricate light-emitting diodes$^1$ and field-effect transistors$^2$ that may greatly extend applications of GaN-based materials.

Further exploitation of devices based on GaN nanomaterials such as nanorods and nanowires has attracted a great deal of attention as these nanosized GaN materials are expected to exhibit superior optical and electrical properties that may greatly extend applications of GaN-based materials. More recently, various forms of GaN nanomaterials have been used to fabricate light-emitting diodes$^1$ and field-effect transistors$^2$ that may greatly extend applications of GaN-based materials.
GaN because it lies in the phonon band gap between the acoustic and optical bands of GaN. The peak, therefore, cannot be explained even with disorder-activated Raman scattering and indeed it is not observed in either experimentally measured or theoretically calculated Raman spectra of amorphous GaN.9,12

Figure 2 shows the Raman spectra of Ga2O3 nanowires nitrided at 750, 800, and 950 °C, respectively, under identical ammonia gas flow for 30 min. The typical Raman spectrum of pure β-Ga2O3 nanowires is also plotted for reference. In the reference spectrum, the sharp peaks stem from the different vibrational modes of β-Ga2O3 except for the 520 cm−1 peak of the Si substrate marked by an asterisk. From Fig. 2, one can clearly observe the evolution of the four GaN-related Raman peaks at 252, 418, 564, and 720 cm−1 indicated by vertical arrows. These peaks start to show up in the Raman spectrum of the Ga2O3 nanowires nitrided at 750 °C and gradually become dominant with increasing nitridation temperature. It is particularly interesting to note that the 418 cm−1 peak evolves from the Raman peak of β-Ga2O3 at 416 cm−1. This provides an important clue about the microstructural origin of the 418 cm−1 peak.

Figure 3(a) shows a representative high-resolution transmission electron microscopy (HRTEM) image of a Ga2O3 wire nitrided at 750 °C. The horizontal fringes parallel to the wire axial direction are found to dominate in the image and have a spacing of about 2.81 Å which corresponds to the d spacing of the β-Ga2O3 [002] lattice planes. These facts indicate that the majority of the wire is still β-Ga2O3 although it was nitrided at 750 °C. However, these horizontal fringes do not coherently prolong throughout the entire wire and are broken by many local blurred regions. These regions are believed to be the disordered grains where nitrogen atoms are already incorporated into the lattice of β-Ga2O3. Such a grain is indicated by a rectangle in Fig. 3(a). Besides the blurred regions, the lattice fringes in some local regions are clearly seen to be tilted at angles of 60° and 120° with respect to the [100] direction. We would like to point out that no corresponding lattice planes of the β-Ga2O3 phase possess such tilting directions or spacing between the tilting fringes. Furthermore, strong distortion of the horizontal fringes can be seen in these regions. For example, in such a region outlined by the elliptical line in Fig. 3(a), the oblique fringes become prominent and the horizontal fringes are significantly distorted. All these structural features can be well interpreted by the incorporation of nitrogen into the local regions. The inset in Fig. 3(a) shows the selected area electron diffraction (SAED) pattern of such a region. Interestingly, the hexagonal diffraction pattern can be seen although it is dimmed by the strong disorders in the region. It can be viewed as further supporting evidence of nitrogen incorporation into local Ga2O3 lattice regions. We thus conclude that the 750 °C nitridation in our case has led to the N incorporation and formation of local Ga–N bonds inside β-Ga2O3 lattice. Increasingly blurred regions with irregularly oriented fringes are thus expected in HRTEM images of the Ga2O3 nanowires nitrided at higher temperatures. Indeed, such expectation is verified in the two HRTEM images of the Ga2O3 nanowires nitrided at 800 °C, as shown in Figs. 3(b) and 3(c). This concurs with the observation of N incorporation made by one of us using x-ray photoelectron spectroscopy and photoluminescence measurements.13 In the local inclusions embedded into β-Ga2O3, the Ga–N bond configuration may be significantly different from the normal configuration in the GaN wurtzite phase. Two kinds of Ga–N bond configurations are postulated: one is GaN-like and the other Ga2O3-like. GaN-like bonds exhibit vibrational properties which can be interpreted using the VDOS of GaN. For Ga2O3-like Ga–N bonds, however, different vibrational properties such as the observed 418 and 252 cm−1 peaks are to be expected. It is known that the wurtzite-GaN lattice can be referred to as an arrangement of corner-sharing Ga–N4 tetrahedra, whereas β-Ga2O3 consists of mixed edge-sharing Ga–O6 octahedra and corner-sharing Ga–O4 tetrahedra.14 The unique mixed bond configurations of β-Ga2O3 crystal thus give rise to more vibration modes than the pure wurtzite phase, as shown in the bottom Raman spectrum in Fig. 2. For instance, the 416 cm−1 peak is an intrinsic vibration mode exactly associated with the Ga–O6 octahedra in the β-Ga2O3.
lattice. During the nitridation of $\beta$-Ga$_2$O$_3$ nanowires, N atoms are expected to replace O atoms either in Ga–O$_4$ or in Ga–O$_6$ bond configurations. The latter replacement will result in the formation of normal Ga–N$_4$ bonds while the former may lead to the formation of local Ga–N$_6$ octahedral structures. Of course, it should be pointed out that local Ga–N$_6$ structures with $6 \geq x > 4$ might exist due to incomplete replacement chemical reaction during the nitridation process. These resultant N-rich local structures should bring about some fresh peaks in the Raman spectrum. As shown in Fig. 2, the close relationship between the 418 cm$^{-1}$ peak of the GaN nanowires and the 416 cm$^{-1}$ peak from the Ga–O$_6$ octahedral structure of $\beta$-Ga$_2$O$_3$ gives strong support for the existence of local Ga–N$_6$ octahedral structures. As the nitridation temperature is increased, more Ga–O$_6$ octahedral structures transform into the Ga–N$_6$ bond structures, resulting in an increase of the 418 cm$^{-1}$ peak in the Raman spectrum, as observed in Fig. 2. However, when the nitridation temperature is high enough, unstable Ga–N$_6$ bonds will change into stable Ga–N$_4$ bonds. This accounts for the reduction of 418 cm$^{-1}$ Raman peak intensity from the samples nitrided at 950 C and above. Such an argument is supported by additional experimental spectra as presented below.

Figure 4 depicts three Raman spectra of Ga$_2$O$_3$ nanowires nitrided at higher temperatures. The top and middle ones are the Raman spectra from the samples nitrided in ammonia at 1100 °C for 20 and 30 min, respectively, while the bottom is from a sample nitrided at 1150 °C for 20 min. The Raman signals from Ga$_2$O$_3$ components are no longer observed in these spectra, indicating that almost complete nitridation of Ga$_2$O$_3$ has occurred under these conditions. In comparison with the top and bottom spectra, the 418 cm$^{-1}$ peak for the middle spectrum that corresponds to the longer nitridation time is greatly enhanced. This implies that increasing nitridation time favors the formation of the unstable Ga–N$_6$ bonds giving the 418 cm$^{-1}$ peak. However, higher treatment temperature results in the transformation of the unstable Ga–N$_6$ bond structure to the stable Ga–N$_4$ phase, as indicated by the bottom spectrum in Fig. 4. Here, the peak at 565 cm$^{-1}$, which corresponds to the $E_2$ (high) mode of hexagonal crystalline ZnO, becomes sharper and more dominant, indicating a higher quality hexagonal phase of ZnO.

From the discussions given above and the structural nature of octahedral structure, the formation of Ga–N$_6$ bond structures requires two conditions, namely, a nitrogen rich condition and a local loosened lattice environment. In fact, all the GaN nanostructures reported in the literature showing the 418 cm$^{-1}$ Raman peak were obtained in N$_2$ or NH$_3$ ambience providing an excellent N-rich environment.

Even in the case of ion-implanted GaN, the N-rich local defected structures with the loosened lattice spacing were formed as Ga atoms are more easily displaced than N atoms. In our case, the original $\beta$-Ga$_2$O$_3$ lattice provides an ideal environment for the formation of local Ga–N$_6$ octahedral structures during the nitridation due to the existence of Ga–O$_6$ octahedra, thus explaining the remarkable vibration mode at 418 cm$^{-1}$ in the GaN nanowires as obtained by nitrid ing $\beta$-Ga$_2$O$_3$ nanowires. It is worth mentioning that a reversed phase transition of GaN from tetrahedrally bonded structure to an octahedrally bonded structure under high pressure has been realized.

We also note that in an earlier theoretical work done by Sun et al., it was pointed out that “nonbonding” lone pairs exist on the nitride surface and can lower the Raman frequencies of vibration modes. The experimental results presented in the present study seem consistent with their theoretical prediction although there is no quantitative estimation of the Raman frequency shifts available.

In conclusion, we have shown that the vibrational mode at 418 cm$^{-1}$ frequently observed in GaN nanostructures most likely originates from octahedrally bonded GaN structures. This conclusion is strongly supported by the observed evolution of the 418 cm$^{-1}$ mode under postnitridation conditions of $\beta$-Ga$_2$O$_3$ nanowires grown on Si substrates.

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