

Abnormal pressure-induced structural transformations of gallium nitride nanowires

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One-dimensional nanostructured GaN was studied at pressures up to 65 GPa by *in situ* synchrotron x-ray diffraction. A wurtzite-to-rocksalt transformation was observed at ~ 55 GPa, an onset pressure higher than that for bulk GaN, but lower than that for nanocrystalline GaN. Such transformation was found extremely incomplete even at the highest pressure but was facilitated by decompression. In addition, GaN nanowires exhibited drastically different volume responses to compression than did GaN in other forms. These unusual pressure behaviors of GaN nanowires are attributed to the interplay of several factors involving the intrinsic nanoproperties and the compression conditions. © 2010 American Institute of Physics. [doi:10.1063/1.3394009]

Gallium nitride (GaN) is a wide band gap semiconductor of great technological importance.¹ Due to the high degree of hardness, low compressibility, high ionicity, and high thermal conductivity, GaN has been considered as a promising candidate for optoelectronic devices operating under extreme conditions such as high pressure.² It is well established that GaN transforms from a wurtzite (B4) structure ($P6_3mc$) to a rocksalt (B1) structure ($Fm\bar{3}m$) at high pressures.^{3–11} However, there were large discrepancies in the reported transition pressures (e.g., 42–54 GPa for experimental results^{4,7,12} and 37–55 GPa for other theoretical studies^{3,13–17}). GaN can also be synthesized in the nanocrystalline form, either as nanowires or as quantum dots.^{9,18,19} Compared to bulk GaN, nanostructured GaN exhibits attractive properties and thus enhanced performance for applications such as optoelectronic devices because of its excellent tunability of its direct band gap.²⁰ Therefore, studies on structural tuning of nano-GaN, such as by the application of pressure in comparison with the bulk materials, are of fundamental interest.²¹ To date, only Jorgensen *et al.*⁹ have investigated the phase transformations and compressibility of GaN nanocrystals in comparison with the bulk GaN. In this paper, we report the *in situ* high-pressure x-ray diffraction investigation of one-dimensional nanostructured GaN in the form of zigzagged nanowires where unusual pressure behaviors were observed.

The GaN nanowires were synthesized by passing ammonia through a mixture of Ga and Ga_2O_3 at a high temperature using Au nanoparticles as the catalyst.¹⁹ The scanning electron microscopy (SEM) images [Fig. 1(a)] revealed that the GaN nanowires had a wirelike structure comprised of zigzag periodic units with a length of tens to hundreds of microns and a thickness of several tens of nanometers. The synchrotron angle-dispersive x-ray diffraction measurements were performed using an incident wavelength of 0.3680 Å and a beam size of $15 \times 10 \mu m^2$. GaN nanowires were compressed up to 65 GPa using a symmetric diamond anvil cell. Silicone oil was used as the pressure-transmitting medium and pressure was determined by the ruby fluorescence method.

Selected x-ray diffraction patterns of GaN nanowires are shown in Fig. 2. The diffraction pattern at near ambient pressure (i.e., 0.5 GPa) can be indexed with a hexagonal wurtzite structure ($P6_3mc$) with cell parameters consistent with the previous diffraction measurement of GaN nanowires.¹⁹ In contrast to the diffraction pattern of nanocrystalline GaN, which is characterized by significantly broadened reflection profiles,⁹ however, the narrow and sharp reflections for GaN nanowires observed here suggest an excellent crystalline phase that resembles bulk GaN. Upon compression, the wurtzite phase was found to persist to 65 GPa as indicated by the consistent indexing of the first six reflections associated with this phase. At 55 GPa, a new reflection appeared at 10.4519° , which can be indexed as (2 0 0) for the rocksalt phase, suggesting the onset of a phase transformation. We note that the phase transition pressure of 55 GPa was higher

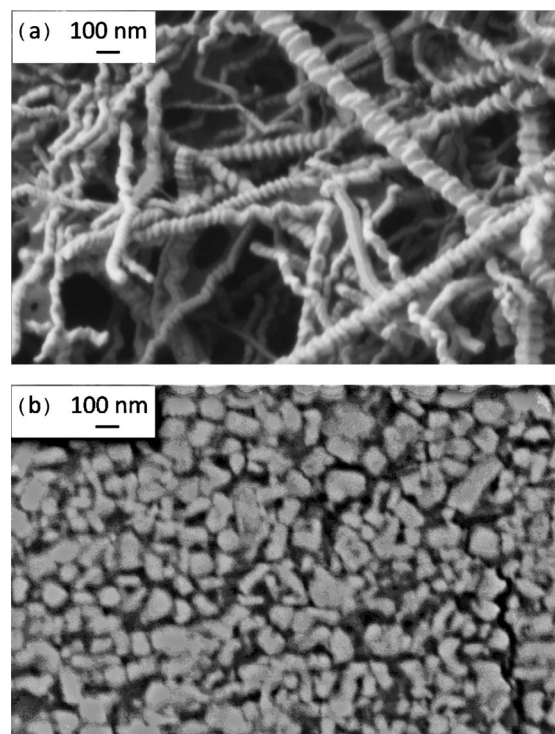


FIG. 1. SEM images of GaN nanowires before compression (a) and after decompression (b) with scales labeled in each panel.

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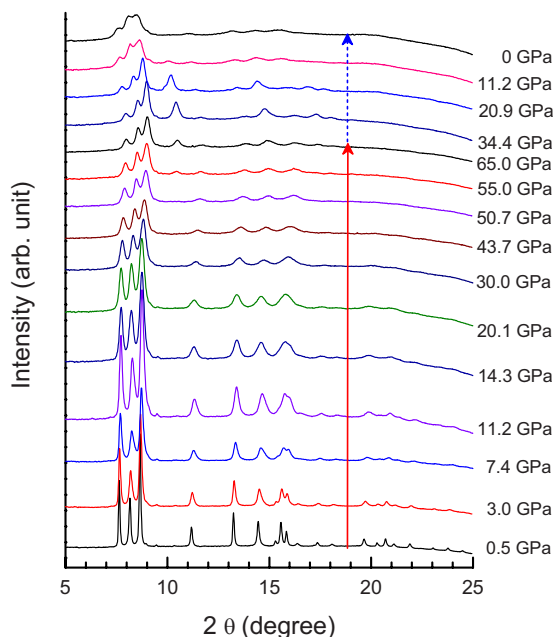


FIG. 2. (Color online) X-ray diffraction patterns ($\lambda=0.3680 \text{ \AA}$) at selected pressures. The solid and dashed arrows indicate the compression and decompression sequence.

than that in most of the previous studies for bulk GaN^{5,7} but lower than that for nanocrystalline GaN (i.e., $\sim 60 \text{ GPa}$).⁹ Size and morphology-dependent enhancements of transition pressures have been observed in other nanostructured materials.²¹ Currently it is the general understanding that surface energy plays an important role in nanostructures and contributes to the enhanced transition pressures. The GaN nanowires in the current study had an initial wirelike morphology and converted to smaller nanoparticles upon compression with an average size of 50–200 nm [Fig. 1(b)], which resulted in an increased surface area. Comparing with the particle size of the nanocrystalline GaN (i.e., 2–8 nm) studied previously,⁹ it can be inferred that the surface energy of GaN increased from bulk to nanowires and to nanoparticles with decreasing sizes, giving rise to the corresponding different transition pressures.

Another significant difference from previous studies is that the wurtzite-to-rocksalt transformation for GaN nanowires was far from complete even at 65 GPa. Rietveld analysis of the GaN nanowire diffraction pattern at 65 GPa shown in Fig. 3 indicates that the wurtzite and rocksalt phases coexist at this pressure with a respective abundance of 88% and 12%. In contrast, an abundance of almost 100% was reported for the rocksalt phase of bulk GaN at a pressure of less than 60 GPa in most of the previous studies.^{4,7,8,12} Our observation was consistent with that for nanocrystalline GaN where the wurtzite to rocksalt phase transition was found to be incomplete even at 63.5 GPa.⁹ Similar results were also obtained in other one-dimensional nanomaterials, such as boron nitride nanotubes.²² In addition to the intrinsic properties of nanostructures, nonhydrostaticity due to use of silicone oil as the pressure-transmitting medium may also contribute to the “sluggish” phase transformations, as manifested by the significant broadening of all the reflections especially at high pressures. Furthermore, severe distortions in the Debye-Scherrer two-dimensional diffraction patterns were observed in the high-pressure region (not shown), indicating a pressure-induced enhancement of the lattice strain. All of

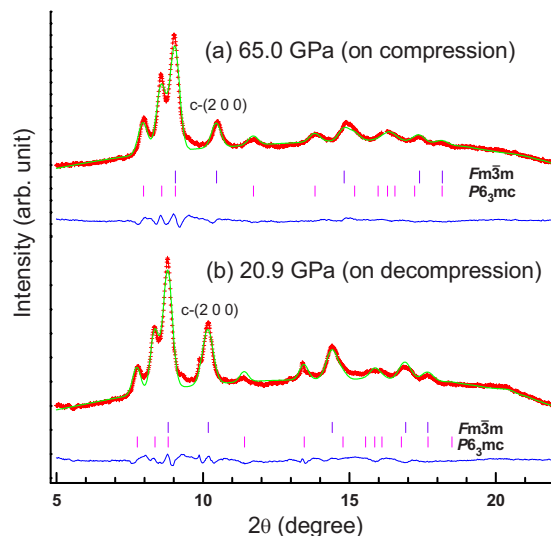


FIG. 3. (Color online) Rietveld refinement of the x-ray diffraction patterns for GaN nanowires at (a) 65 GPa on compression and (b) 20.9 GPa on decompression. The red cross is experimental x-ray intensity and the green line is the calculated diffraction patterns based on refinement with the blue curve at the bottom showing the difference between the calculated and observed intensities. The vertical bars denote the indexed reflections for each phase with the space groups labeled beside. The characteristic reflection for the cubic rocksalt phase is labeled as $c-(2\ 0\ 0)$.

these factors may interactively affect the phase stabilities and thus the extent of transformations.

An interesting and unusual phase transformation was observed during decompression. Upon releasing the pressure from 65 GPa, the abundance of the rocksalt phase was found to increase significantly. For instance, Rietveld refinement [Fig. 3(b)] suggested that the fraction of the rocksalt phase had increased from 12% at 65.0 GPa to 29% at 20.9 GPa upon releasing the pressure. Below 20.9 GPa, the rocksalt phase gradually retransformed to the wurtzite phase, and was retained even at very low pressures (e.g., $< 16.4 \text{ GPa}$). The recovered phase at ambient pressure can be identified as a single wurtzite phase, but the significantly broadened diffraction pattern suggests a pressure-induced reduction in the grain size, consistent with the SEM result [Fig. 1(b)]. All of the previous studies found that the B4–B1 phase transformation was reversible for both bulk GaN and nanocrystalline GaN^{4,8,12} indicating that the wurtzite phase was thermodynamically stable in the low pressure region. However, the strongly contrasting, unprecedented decompression behavior of the GaN nanowires characterized by a large hysteresis, suggests that the rocksalt phase is a metastable phase. Prominent hysteresis was likely associated with different kinetic barriers that impeded the sharp transitions often involving a metastable phase.²¹

Finally, the unit cell volume of GaN nanowires for the wurtzite phase was plotted against the pressures shown in Fig. 4 in comparison with previous studies. The P-V curve of GaN nanowires exhibited a noticeable discontinuity in the pressure region of 11–20 GPa. The previously established equation of states (EOS) for bulk GaN ($B_0 = 187\text{--}237 \text{ GPa}$)^{7,9} and for nanocrystalline GaN ($B_0 = 319 \text{ GPa}$)⁹ suggest that the bulk modulus for GaN nanowires in the pressure region above 20 GPa can be estimated to be somewhere in between, consistent with that an increase in the surface area may enhance the bulk modulus. This observation can be further understood from the fact the GaN

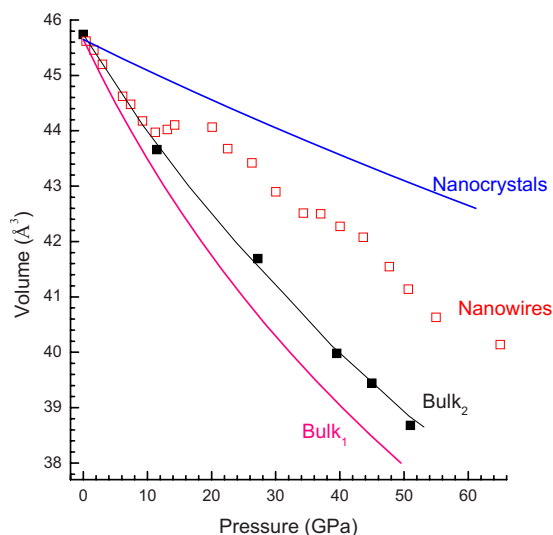


FIG. 4. (Color online) Unit cell volume as a function of pressure for GaN nanowire (open squares) in comparison with that for bulk and nanocrystal GaN. Solid lines are fitted EOS curves for bulk GaN using bulk moduli of 187 GPa (bulk₁) and 237 GPa (bulk₂) from Refs. 9 and 7, respectively. The dashed line is fitted EOS curve for nanocrystalline GaN using bulk modulus of 319 GPa from Ref. 9.

nanowires break into nanoparticles when the external stress surpasses the yield strength at around 20 GPa, resulting in the size-induced enhancement of the bulk modulus. The correlation between the reduction in the particle size and the increasing bulk modulus has been found in other nanomaterials, such as AlN nanocrystals.²³ A similar discontinuity was also found in the P-V curve for nanocrystalline CeO₂.²⁴ However, a decrease in the bulk modulus of nanocrystalline CeO₂ was found above ~20 GPa, a pressure that was believed to signify the onset of a size-induced weakening of the elastic stiffness of nanocrystalline CeO₂. Therefore, the discontinuity in the EOS for both nanocrystalline CeO₂ and GaN nanowires can be understood from the nanosize effect while the different shapes of the EOS curves may be associated with opposite pressure-induced changes in particle size. It is probable, too, that the P-V behavior observed in the region of 11–20 GPa is associated with the combined effect of the original nanowires and the yield-generated nanoparticles. The high yield strength observed in the GaN nanowires thus furthers the understanding of the morphology-tuned improvement in yield strength and hardness in hard materials applications. Moreover, the choice of silicone oil as the pressure-transmitting medium may also contribute to the discontinuity observed in the P-V curve. An anomalous behavior inherent in silicone oil at ~12 GPa, which is believed to be the result of a phase transition,^{25,26} seems to have further complicated the abnormal behavior of GaN nanowires in the pressure region of 11–20 GPa. It would therefore be interesting to use better pressure transmitting media, such as helium, to study the compressibility of GaN nanowires under hydrostatic conditions.

In summary, we have investigated the high-pressure structures and properties of the one-dimensional nanostructured GaN using *x*-ray diffraction *in situ*. A wurtzite to rocksalt phase transformation was observed to start at 55 GPa but was still far from complete even at pressures of up to 65 GPa. Upon decompression, the abundance of the rocksalt phase was found to first increase and then to decrease until the ambient pressure was reached, at which time only the

wurtzite phase was recovered, indicating a reversible transformation but with a large hysteresis. A discontinuity in the EOS for GaN nanowires was found in the pressure region of 11–20 GPa. These abnormal pressure behaviors of GaN nanowires were compared with those obtained in previous high pressure studies of bulk and nanocrystalline GaN and can be attributed to the nano-size and morphology-dependent thermodynamic and kinetic properties of the GaN nanowires with the additional complication of the nonhydrostatic conditions.

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