Tensile Deformation of Tubular Structures of Nitride-based Nanotubes: Brittle and Weak Behavior

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Abstract

This study adopts classical molecular dynamics (MD) simulation with the realistic Tersoff many-body potential model to investigate the mechanical properties of gallium nitride (GaN) nanotubes. The investigation focuses primarily on the mechanical properties of (\(n, 0\)) and (\(n, n\)) GaN nanotubes since these particular nanotubes represent two extreme cases. The present results indicate that under small strain conditions, the mechanical properties such as Young’s modulus are insensitive to the wrapping angle. Conversely, the wrapping angle has a significant influence upon these mechanical properties under large strain conditions. It is demonstrated that (9, 0) GaN nanotubes are far less resistant to bond rotation. Under large tensile strain conditions, due to the unfavorable bond orientations induced by Stone-Wales (S-W) transformation, the bonds in (\(n, 0\)) GaN tubes quickly degenerate.

Key Words: Gallium Nitride Nanotube, Stone-Wales Bond Rotation

1. Introduction

Following their initial discovery by Iijima, carbon nanotubes (CNTs) have been the subject of intense research interest and activity [1]. More recent studies have reported non-carbon nanotubes composed of significant chemical compositions. Many researchers have investigated gallium nitride (GaN) nanotubes. For example, Joshua and Rongrui [2] proposed an “epitaxial casting” approach for the synthesis of single-crystal GaN nanotubes. Meanwhile, Seung and Young [3] employed density-functional calculations to investigate the structural stability and electronic characteristics of GaN nanotubes, and showed that these characteristics resembled those of conventional carbon nanotubes. Both computer-assisted and experimental studies have tended to focus primarily on the electronic behavioral aspects of nanotubes. Furthermore, the mechanical properties of GaN nanotubes are important because potential applications depend on their stability and stiffness. However, a review of the available literature reveals that relatively few investigations have been conducted into the full range of mechanical properties of GaN nanotubes. Specifically, no studies have considered the particular case of GaN nanotube response beyond the elastic limit threshold or during plastic deformation. This study considers a particular set of GaN nanotubes whose phases are such that the tubes are as stable as carbon nanotubes. Classical molecular dynamic (MD) simulations based on the Tersoff potential [4–6] model are employed to perform a thorough investigation into the mechanical properties of these promising GaN nanotubes.

2. Molecular Dynamics

This study investigates the mechanical properties of graphitic GaN nanotubes under tension and fatigue us-
ing the Tersoff many-body potential function [4–6]. The current simulations employ the parameters fitted by Benkabou et al. [7]. Specifically, the present simulations consider a family of GaN nanotubes of virtually identical radius \{(5, 5), (6, 4), (7, 3), (8, 2), and (9, 0)\}, and zigzag \((n, 0)\) GaN nanotubes, where \(5 \leq n \leq 9\). The structures of typical \((9, 0)\) armchair and \((5, 5)\) zigzag GaN nanotubes are presented in Figure 1. Additionally, several researchers have successfully predicted the nanoscale opto-electronic and electronic properties of GaN nanotubes [8]. However, relatively few detailed investigations into the full range of mechanical properties of these nanotubes under remarkable conditions such as tension have been performed. The present study simulates the annealing of GaN nanotubes at a specific temperature over a period of \(10^6\) time-steps, and imposes periodic boundary conditions in the axial direction.

3. Results and Discussion

3.1 Mechanical Properties of GaN Nanotubes

The present theoretical investigations of GaN nanotubes are restricted primarily to the comparison and contrast of the mechanical behaviors of \((n, 0)\) and \((n, n)\) GaN nanotubes with those of carbon nanotubes with similar radii. To compare the behaviors of the different tubes, parabolic fits to the two sets of data in the linear elastic response regime are used to compute the corresponding Young’s modulus. In this tensile study, a change of strain of 0.5% was followed by a MD relaxation of \(10^6\) time-steps for a strain rate of \(10^{13}/\text{ps}\). It is noted that the linear elastic response regime is limited to low applied strains \((\leq 8\%)\) and that no plastic structural deformation takes place in this regime. The Young’s modulus is calculated as the second derivative of the total energy with respect to the strain at the equilibrium configuration (i.e. at zero strain), i.e.

\[
Y = \frac{1}{V_0} \left( \frac{\partial^2 E}{\partial \varepsilon^2} \right)_{\varepsilon=0}
\]

where \(V_0\) is the equilibrium volume, \(\varepsilon\) is the strain, and \(E\) is the total energy. For a single-walled carbon nanotube (SWCNT), the equilibrium volume can be defined as the volume of a hollow cylinder, i.e.

\[
V_0 = 2\pi LR\delta R
\]

where \(L\) denotes the length of the CNT, \(R\) is the radius, and \(\delta R\) is the thickness (i.e. \(\sim 3.4\text{Å}\)). Previous studies have defined the thickness of the CNT using a variety of different expressions. However, it is difficult to determine the value of \(V_0\) for a GaN nanotube. The symmetrically unconstrained Ga-N bond rotation which occurs as a result of the structural relaxation causes the generation of a “sawtooth” or “rippled” surface as the Ga atoms move toward the tube axis while the N atoms move simultaneously in the opposite direction. These bond rotation effects cause the definition of shell-thickness for the GaN nanotube to be ill-defined. However, for the sake of simplicity, the bond rotation effects are ignored in the present study. Although this practice may introduce some degree of error, this simplification is reasonable in the present qualitative investigation, whose purpose is simply to compare the mechanical behavior of GaN nanotubes with that of their carbon counterparts. Additionally, the Poisson ratio is calculated as the negative ratio of the relative change in radius over the relative elongation, i.e.

\[
\nu = -\frac{R(\varepsilon) - R_0}{R_0}
\]

where \(R(\varepsilon)\) is the tube radius at strain \(\varepsilon\), and \(R_0\) is the equilibrium \((\varepsilon = 0)\) strain.

Figure 2 presents the variation of strain energy per atom under the linear elastic response regime, calculated as the difference between the total energy per atom in the strained and unstrained conditions, with the percentage strain. Table 1 presents the calculated mechanical properties of the GaN and carbon nanotubes considered in the current study. It can be seen that the Young’s modulus of 0.721 TPa for the \((9, 0)\) GaN nanotube is approximately 73% of that for a similar carbon nanotube (~1 TPa). The
calculated Young’s moduli of the carbon nanotubes are almost consistent with the \( O(N) \) tight-binding results presented previously by Ozaki et al. [9]. It is noted that the Young’s moduli of the GaN nanotubes are clearly lower than those of the conventional carbon nanotubes. This observation can be attributed to various differences in the bond properties between the carbon nanotube and GaN nanotube. For example, the C-C bond is known to be stronger than the Ga-Ga, N-N, and Ga-N bond and it is reasonable to assume that in a low-dimensional structure such as a nanotube the same property must appear.

Figure 2 demonstrates that at smaller strains, the parabolic curves of the \((n, 0)\) and \((n, n)\) GaN nanotubes virtually overlap, but that at higher strains the two curves diverge. A similar trend is also noted for the carbon nanotubes. Under small strains, the Young’s moduli of the two extreme GaN nanotubes are almost identical. This insensitivity to the helicity effect is consistent with the results reported for carbon nanotubes [10,11]. However, the strain energy under large strain conditions shows a significant sensitivity to the wrapping angle. As described later in this paper, the significant difference in mechanical behavior can be explained by carefully examining the structural properties in the vicinity of the bond rotation transformations.

### 3.2 Effect of Helicity on Larger Tensile Deformations of GaN Nanotubes

Both GaN and carbon nanotubes respond elastically until they undergo catastrophic deformation at a certain critical strain. Beyond this strain, it is found that the bonds rotate significantly from a predominantly circumferential direction to a mainly axial direction. This bond rotation causes the tube to elongate along its axis while simultaneously shrinking in the perpendicular direction. Such bond rotations, which are known collectively as Stone-Wales (S-W) transformation [12], transform four hexagons into two pentagons and two heptagons, as shown in Figure 3.

Table 1 indicates that both the GaN and carbon \((n, n)\) nanotubes have a slightly higher stiffness to the current failure model than the \((n, 0)\) tubes of similar radii, i.e. the effectiveness of the partial strain relief induced by bond rotation depends strongly on the wrapping angle. As shown in Figure 3, the S-W transformation contains two clearly identifiable bond rotation defects within one unit cell. Specifically, the Ga-Ga and N-N bonds are either aligned predominantly along the axial direction or along the circumferential direction after bond rotation. Figure 3(a) shows the particular arrangement of bonds in an \((n, 0)\) GaN nanotube, and indicates that the two bonds align perfectly with the axial direction in one unit S-W defect area [the marked bonds in Figure 3(a)]. These bonds are stretched under maximum stress and hence are more susceptible to subsequent breakage. Hence, an \((n, 0)\) GaN nanotube has the most-stretched bond is clearly observed in the process of breaking. Conversely, in the \((n, n)\) GaN nanotube.  

### Table 1. Mechanical properties of the GaN and carbon NTs

<table>
<thead>
<tr>
<th>Tube Type</th>
<th>Diameter (nm)</th>
<th>( Y ) (GPa)</th>
<th>( \sigma_{\text{max}} ) (Ev/Å)</th>
<th>( \epsilon_{\text{critical}} ) (%)</th>
<th>( v )</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN (5, 5)</td>
<td>0.847</td>
<td>793</td>
<td>4.25</td>
<td>14.6</td>
<td>0.263</td>
</tr>
<tr>
<td>GaN (9, 0)</td>
<td>0.881</td>
<td>721</td>
<td>3.43</td>
<td>13.3</td>
<td>0.221</td>
</tr>
<tr>
<td>C (7, 7)</td>
<td>0.834</td>
<td>984</td>
<td>8.12</td>
<td>17.6</td>
<td>0.296</td>
</tr>
<tr>
<td>C (11, 0)</td>
<td>0.856</td>
<td>976</td>
<td>6.57</td>
<td>16.3</td>
<td>0.272</td>
</tr>
</tbody>
</table>

Figure 2. Variation in strain energy with axial tension for two extreme GaN NTs (solid line), and for carbon NTs (dotted line).
nanotube, no bonds align exactly along the axial direction. As a result, the stress is distributed across the four bonds [marked bonds in Figure 3(b)] around the defect area, and no bond breakage is evident. The structures of $(5, 5)$ and $(9, 0)$ GaN nanotubes during the tensile deformation procedure at constant temperature of $T = 300 \text{ K}$ are shown in Figure 4. The SW defect in GaN nanotubes generally generates the less favorable homo-elemental bonds such as Ga-Ga and N-N bonds. The high energy cost of the frustrated Ga-Ga and N-N bonds causes GaN nanotubes to be structurally unstable. However, in the case of GaN nanotubes the SW defect appears to reduce the high stress caused by the geometrical strain, despite the Ga-Ga and N-N bonds. Finally, the formation of the SW defect leads to the fracture of the GaN nanotubes. In an $(n, 0)$ GaN nanotube with up to 17% tensile strain, slight bond breakage is observed, whereas no such breakage is evident in an $(n, n)$ GaN nanotube of equivalent radius. Therefore, although a weakness is evident in the S-W defect area in both GaN nanotubes, the effects of S-W transformation are more significant in the $(n, 0)$ GaN nanotube than in the $(n, n)$ GaN nanotube. Additionally, it is also noted that the carbon nanotubes have higher stiffness than the GaN nanotubes since they retain their “perfect” smooth geometric surface after the annealing process, whereas the lower symmetry of the GaN nanotubes tends to inhibit strain relief. Furthermore, even though S-W bond rotation defects are generated, the general carbon nanotubes are relatively robust and can sustain an elongation beyond that of the elastic limit without bond breakage. Conversely, the presence of such defects in the GaN nanotubes causes the structure to become very susceptible to bond breakage under the larger tensile strain considered in the present investigation. This observation can be attributed to the partially ionic nature of the GaN bonding, which reduces the robustness of the nanotube structure. Under some conditions, bond rotation can create unfavorable Ga-Ga and N-N neighbors. The presence of such homo-elemental bonds substantially weakens the entire stiffness. Compared to the case presented above, only one favorable bond rotation pattern exists for carbon nanotubes after S-W transformation (Figure 3(c)). The current S-W transformations of the carbon nanotubes are virtually all in good agreement with the previous studies by Yakobson et al. [13,14]. However, the situation is rather more complicated for GaN nanotubes since the two types of bond ro-

Figure 3. Comparison of bond rotation defects: (a) $(n, 0)$ GaN NT; (b) $(n, n)$ GaN NT; and (c) $(n, 0)$ and $(n, n)$ carbon NT.

Figure 4. Tensile deformation procedure of (a)–(d) $(5, 5)$ GaN nanotubes at constant temperature of $T = 300 \text{ K}$. (The SW defect is denoted by the darker atoms).
ation defects in one unit cell are located on opposite sides of the tube in order to balance the strain.

4. Conclusions

This study has adopted the Tersoff many-body potential to perform MD simulations of the tension testing of a series of nitride-based (GaN) and carbon nanotubes with virtually identical radii. Specifically, this study has clarified the influence of mechanical behaviors upon helicity effect under elongations, respectively. The present investigation validates the majority of the predictions of simpler theories, and points out the limits of their applicability. The following conclusions can be drawn from the current results:

1. The mechanical properties of nitride-based (GaN) and carbon nanotubes can be investigated and compared using the Tersoff many-body potential.
2. The mechanical properties, e.g. the Young’s modulus, are sensitive to the effect of helicity under such conditions as large strain conditions.
3. The present results reveal that carbon nanotubes have somewhat higher Young’s modulus than nitride-based (GaN).

References


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