Electronic Structures of GaN Nanotubes

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Density functional calculations are used to predict the electronic structures of GaN nanotubes. The graphitic GaN is an indirect band gap material with valence band maximum at \(K\) edge. Zigzag nanotube is a semiconductor with direct band gap, whereas armchair nanotube has an indirect band gap along the tube axis. The band gaps decrease with the decreasing diameter, contrary to the case of carbon nanotubes.

I. INTRODUCTION

Carbon nanotubes have been synthesized during the formation of fullerenes using arc discharge of graphite rods [1]. Recently single-wall carbon nanotubes have been produced with high yields by the laser vaporization of graphite powders mixed with small amount of transition metals [2–4]. Since then, researches on carbon nanotubes have been activated. The physical properties of carbon nanotubes as denoted by \((n,m)\) are correlated with their diverse phases. Armchair \((n,n)\) carbon nanotubes are metallic [5,6], while zigzag \((n,0)\) carbon nanotubes are semiconductors with a finite band gap except the case of \(n−m=3k\) \((k:\text{integer})\) which is a small band gap semiconductor [7]. Energy gap can be controlled by varying the diameter, thus allowing band gap engineering [5,8]. Strong electron field emission from carbon nanotubes have been observed, suggesting the applicability to flat panel displays [9,10]. Despite such efforts, applications of carbon nanotubes to memory devices and quantum transport devices are still challenging.

Efficient blue light-emitting diodes have been realized with GaN materials, making its application to full color displays promising [11]. In addition, GaN exhibits considerable hardness, high thermal conductivity, and little radiation damage, suggesting the applicability to high power and high temperature microelectronic devices. Although \(\text{In}_x\text{Ga}_{1−x}\text{N}\) has been tried for band gap engineering by varying In composition, it is still difficult to grow and control high In compositions due to the strain between InGaN and substrate [12]. Therefore, a new form of GaN structure is always desirable if possible.

In this report, we propose a new phase of GaN, a nanotube, using a density functional (DF) calculations. We will show that GaN nanotubes are as stable as carbon nanotubes and can be synthesized under some extreme conditions. Pure boron-nitride and boron-carbon-nitride nanotubes have been successfully produced by arc-discharge [13,14]. The existence of BN-nanotubes suggests the possibility of other nitride nanotube synthesis such as CN and GaN. The present calculations show that the strain energy costs to wrap up graphitic GaN sheets into nanotubes are comparable with those of carbon nanotubes, ensuring again the possibility of GaN nanotube formation. Yet, the initial nucleation seeds for GaN nanotube formation will play a crucial role. The idea of using carbon nanotubes as a nucleation seed will be discussed in conjunction with edge energies in this report. Band structures reveal that GaN zigzag nanotubes is a semiconductor with a direct band gap, whereas armchair nanotubes have an indirect band gap. The energy gap of GaN zigzag nanotubes decreases with the decreasing tube diameter, whereas that of GaN armchair nanotubes is almost constant over a wide range of the diameter, which is contrary to the case of carbon nanotubes.

II. THEORETICAL APPROACHES

Here we investigate the stability and electronic structures of GaN nanotubes and further discuss possible ways of synthesis. For our calculations we use a plane-
Fig. 1. Typical types of GaN nanotubes; Various phases of GaN: (a) Zincblende, (b) graphitic sheet, (c) (5,5) armchair nanotube, and (d) (9,0) zigzag nanotube. Dark-grey and light-grey spheres indicate Ga atom and N atom, respectively.

wave basis DF calculations within the local-density-approximation (LDA) [15] and the SCC-DFTB code (a self-consistent charge density-functional-based tight binding method). In the LDA calculations, the ionic potentials are described by a norm-conserving nonlocal pseudopotential generated by Troullier-Martins [16] in a separable form of Kleinman and Bylander [17]. Exchange-correlation functions parameterized by the Perdew-Zunger scheme [18] are used. The energy was converged to $0.2 \times 10^{-4}$ eV/atom.

The SCC-DFTB method uses a basis of numerically obtained $s$, $p$, and $d$ atomic orbitals. Hamiltonian over-
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III. RESULTS AND DISCUSSION

Various GaN crystal phases exist under different experimental growth conditions [12]. The Wurtzite phase is the thermodynamically stable structure at ambient conditions, whereas the zincblende (ZB) phase (Fig. 1(a)) can be stabilized on various cubic substrates [20,21]. The rocksalt phase can be induced at high pressures [22]. We first calculate the total binding energies of ZB and graphitic GaN phases; zincblende, graphitic, and tube. The values in parentheses in zincblende are from Ref. 12. The terms, $m_e^*$, $m_{h,k}^*$, $m_{h,k}^*$, and $m_{split}^*$ denote the electron, heavy hole, light hole, and (spin-orbit) split-off hole masses, respectively.

<table>
<thead>
<tr>
<th>Structure direction</th>
<th>$m_e^*/m_0$</th>
<th>$m_{h,k}^*/m_0$</th>
<th>$m_{h,k}^*/m_0$</th>
<th>$m_{split}^*/m_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zincblende</td>
<td>$\Gamma$-X</td>
<td>0.17</td>
<td>1.09</td>
<td>1.09</td>
</tr>
<tr>
<td></td>
<td>$\Gamma$-K</td>
<td>0.33</td>
<td>9.54</td>
<td>1.06</td>
</tr>
<tr>
<td></td>
<td>$\Gamma$-L</td>
<td>0.18</td>
<td>3.53</td>
<td>3.53</td>
</tr>
<tr>
<td>Graphitic</td>
<td>$\Gamma$-M</td>
<td>0.08</td>
<td>0.43</td>
<td>0.05</td>
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<tr>
<td></td>
<td>$\Gamma$-K</td>
<td>0.45</td>
<td>1.13</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Table 1. The values of effective mass for several GaN phases; zincblende, graphitic, and tube. The values in parentheses in zincblende are from Ref. 12. The terms, $m_e^*$, $m_{h,k}^*$, $m_{h,k}^*$, and $m_{split}^*$ denote the electron, heavy hole, light hole, and (spin-orbit) split-off hole masses, respectively.

Fig. 5. Band gaps of GaN armchair and zigzag nanotubes as a function of the diameter using the SCC-DFTB and the LDA method. The open circles and open triangles are from the SCC-DFTB. The LDA results (filled circles and filled triangles) after scissor’s operation by comparing the band gap of cubic phase from the LDA with that of experimental value are shown. The energy gap of carbon zigzag nanotubes (open diamonds) are also shown for comparison. The bottom curve shows the energy gap in the case of $n - m = 3k$, where $k$ is an integer. Two characteristic energy gaps are shown in carbon nanotubes as shown in the next curves.
by the DFT-LDA method. We used 28 special $k$-points for cubic GaN and for graphitic GaN in the irreducible Brillouin zone as implemented by Monkhorst and Pack [25]. The kinetic energy cutoff for the plane-wave expansion of wavefunctions is 18 Ry. The band structure for cubic GaN shows a direct band gap, in good agreement with the previous first principles calculations [23]. Heavy hole and light hole bands are degenerate at $\Gamma$ point in zincblende phase. Strong $s$, $p$ hybridization occurs in Ga atoms, whereas large $s$, $p$ splitting occurs in N atoms, i.e., $p$ contributes mostly to the top valence band from 0 to 6 eV and $s$ mostly contributes to the deep band below 12 eV, in excellent agreements with previous calculations [26]. We tested the convergence for the kinetic energy cutoff and $k$-point samplings. The changes in the band structure with more $k$-point samplings were negligible. The band gap of cubic phase is 2.35 eV. With larger kinetic energy cutoff of 29 Ry, the energy gap of cubic GaN saturated to 2.6 eV but no significant changes in the shape of the band structure were found. It is well known that the LDA underestimates the band gap. Better calculations using the GW approximation will simply enlarge the band gap for most wide band gap materials [27].

Graphitic GaN is also a semiconductor with an indirect band gap where the valence band maximum is located at $H$ edge, as shown in Fig. 3(b). The indirect band gap is 2.78 eV, slightly larger than that of the cubic phase, and the direct band gap is 3.49 eV. This can be understood by the Coulomb repulsion between the increased $\pi$ electrons at N sites above the plane.

Wrapping the graphitic sheet into nanotube will require an extra strain energy. The previous calculations show that this strain energy in forming GaN nanotubes is comparable to that of carbon nanotubes, suggesting the existence of the GaN as a form of nanotubes [24,28]. Figure 1(c)-(d) shows armchair (5,5) and zigzag (9,0) GaN nanotubes. Shown in Fig. 4 are the respective band structures along the tube axis. Here we follow the notation of GaN nanotubes similar to the notation employed for carbon nanotubes. There are two inequivalent atoms in the primitive cell of GaN system. We choose (5,5) armchair nanotube with two layers (20 atoms) and (9,0) zigzag nanotube with four layers (36 atoms). The respective diameters are 8.47 and 8.81 Å. The intertube distance is 4.5 Å. The band dispersion at this vacuum separation arising from tube interactions was found to be negligible. It is very interesting to see the differences in the band structures of armchair and zigzag nanotubes. Zigzag nanotubes have a direct band gap, whereas armchair nanotubes have an indirect band gap. The respective band gaps of (5,5) and (9,0) nanotubes are 2.15 and 2.46 eV. The changes in the band structures with more $k$-point samplings (16 $k$-points) were negligible. The valence band maximum of the armchair nanotube is located in the middle of the $\Gamma$-Y. The electronic density of states of both nanotubes are similar to each other.

In order to investigate the diameter dependence of the band gap, we performed the SCC-DFTB calculations for GaN nanotubes of different diameters. The relaxational changes in the atomic configurations were negligible and no buckling was observed, in contrast to BN-nanotubes [29]. The band gap changes slightly with the nanotube length. Therefore we fix the length of the nanotubes to 22 layers. We estimate the convergence of the energy gap dependence on the length of the nanotubes to be within 0.05 eV. Figure 5 shows the band gap for armchair and zigzag nanotubes. Unlike the alternating energy gap of carbon zigzag nanotubes (diamond shape) [24], the band gaps of GaN nanotubes decrease monotonically with the decreasing diameter. The energy gap of $(n, n)$ GaN nanotubes decrease slightly with decreasing the diameter, whereas that of $(n, 0)$ GaN nanotubes decreases significantly with the decreasing diameter. The energy gap converges to the value of the graphitic sheet at large diameter. This decrease of the band gap simply reflects the ionic bonding character, i.e. $s$ and $p$ bands localized to Ga and N respectively are well separated [26]. Wrapping of the graphitic sheet to tubes enhances the rehybridization more seriously in zigzag nanotubes than in armchair nanotubes as the diameter decreases. More $p$ states near the valence band edge and more $s$ states near the conduction band edge are developed at smaller diameter of zigzag nanotubes, as can be seen from the density of states of tubes in different diameters [24].

Our plane-wave DFT-LDA calculations give a energy gap of 2.35 eV for the cubic phase [30], underestimating the experimental value of 3.52 eV [21] by 1.17 eV. The energy gap of the cubic GaN from the LDA in our calculations is 2.35 eV [31], underestimating the experimental value of 3.52 eV [21] by 1.17 eV. It is well known that the LDA approach underestimates the band gap. More sophisticated calculations using GW approximation reproduces the experimental band gap more correctly. For most semiconductors, the scissors operation, simply shifting the band gap, can be applied to predict the correct band gap [32,33]. One may estimate the band gap of GaN nanotubes at infinite diameter. Values of the band gap with correction from the LDA calculations are also shown in Fig. 5. The band gap of graphitic sheet is 2.78 eV. The scissors operation [32,33] gives the corrected band gap of nanotubes at infinite diameter (or equivalently graphitic sheet) of approximately 3.95 eV. We note that energy gaps can be tailored by varying the diameter. This suggests that ultimate nanoscale full color displays can be realized using GaN nanotubes.

We also calculate effective masses of several GaN phases, as shown in Table 1. Our calculations for zincblende phase show good agreement with the previous first principles calculations except electron effective mass at $K$ edge and hole effective mass at $L$ edge [12]. Relatively large errors exist in evaluating the heavy-hole effective masses due to the ambiguity of determining the range of wave vectors which are valid within the effective mass approximation. The electron effective masses decrease with increasing diameter in armchair tubes,
whereas they increase with increasing diameters in zigzag tubes. On the other hand, the hole effective masses behave completely in opposite way, i.e., the hole effective masses increase with increasing diameters in armchair tubes, whereas they decrease with increasing diameters in zigzag tubes.

IV. SUMMARY

We have performed density-functional calculations to investigate electronic structures of GaN nanotubes. The calculations for the total energy reveal that GaN nanotubes are stable and may be formed under some extreme conditions. The energy gap decreases with the decreasing diameter, enabling band gap engineering. The estimated band gap of the GaN nanotubes at infinite diameter is approximately 3.95 eV, which is 0.43 eV larger than that of cubic GaN phase. This strongly suggests that ultimate nanoscale optoelectronic devices for full color displays may be realized with sophisticated modern synthesis techniques. The effective masses of several GaN phases are also calculated.

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REFERENCES

[15] This method is implemented in the CASTEP code which is a registered software product of Molecular Simulations Inc.
[30] We tested the convergence for kinetic energy cutoff and k-point samplings. With larger kinetic energy of 29 Ry, the $E_g$ of cubic GaN saturates to 2.60 eV. The changes with more k-point samplings (16 k-points) were negligible.
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