Stability and electronic structure of GaN nanotubes from density-functional calculations

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Density-functional calculations are used to predict the stability and electronic structures of GaN nanotubes. Strain energies of GaN nanotubes are comparable to those of carbon nanotubes, suggesting the possibility for the formation of GaN nanotubes. The zigzag nanotube is a semiconductor with direct band gap, whereas the armchair nanotube has an indirect band gap. The band gaps decrease with decreasing diameter, contrary to the case of carbon nanotubes. We further discuss possible ways of synthesizing GaN nanotubes in conjunction with carbon nanotubes. [S0163-1829(99)14135-3]

Carbon nanotubes have been synthesized during the formation of fullerenes using arc discharge of graphite.[1] Recently single-wall carbon nanotubes have been produced with high yields by the laser vaporization of graphite powders mixed with a small amount of transition metals.[2–4] 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 for the case of $n\text{-}m=3k$ (k:integer), which is a small band-gap semiconductor.[7] The band gap can be controlled by varying diameter, thus allowing band-gap engineering.[5,8] Strong electron field emission from carbon nanotubes has been observed, suggesting the applicability to flat panel displays.[9,10]

With the advent of epitaxial growth techniques for GaN, efficient blue light-emitting diodes have been realized, making its application to full color displays promising.[11] Although $In_xGa_{1-x}N$ has been tried for band-gap engineering by varying the In composition, it is still difficult to grow and control high In compositions due to the strain between InGaN and the substrate.[12] Therefore, a new form of GaN structure is always desirable if possible.

In this paper, we propose a phase of GaN, a nanotube, using density-functional (DF) calculations. We will show that the GaN nanotube is a metastable state and can be synthesized under some experimental 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 necessary 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 Brief Report. Band structures reveal that GaN zigzag nanotubes are semiconductors with a direct band gap, whereas armchair nanotubes have an indirect band gap. The band 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. Ultimate nanoscale optoelectronic devices for a wide range of wavelengths may be realized using GaN nanotubes.

Here we investigate the stability and electronic structures of GaN nanotubes and further discuss possible ways of synthesis. For our calculation we use a plane-wave basis DF calculation within the local-density approximation (LDA) (Ref. 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 parametrized by the Perdew-Zunger scheme[18] are used. The energy cutoff for

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the plane-wave expansion of wave functions is 18 Ry, and periodic boundary conditions are applied. Brillouin-zone integrations are done using eight special k-points sampling, as suggested by Monkhorst and Pack.[19] The energy was converged to 0.2×10^{-4} eV/atom. The nanotubes are placed 4.5 Å away from each other.

The SCC-DFTB method uses a basis of numerically described s,p, and d atomic orbitals. Hamiltonian and overlap matrix elements are evaluated by a two-center approach. Charge transfer is taken into account through the incorporation of a self-consistency scheme for Mulliken charges based on the second-order expansion of the Kohn-Sham energy in terms of charge-density fluctuations. The diagonal elements of the Hamiltonian matrix employed are then modified by the charge-dependent contributions in order to describe the change in the atomic potentials due to the charge transfer. The off-diagonal elements have additional charge-dependent terms due to the Coulomb potential of ions. Further details of the SCC-DFTB method have been published elsewhere.[20]

Various GaN crystal phases exist under different experimental growth conditions.[12] The wurtzite phase is the thermodynamically stable structure at ambient conditions, whereas the zinc blende phase can be stabilized on various cubic substrates.[21,22] We first calculate the total binding energies of zinc blende and graphitic phases using SCC-DFTB in order to study the relative stabilities. We choose a cubic supercell of 216 atoms for zinc blende GaN and 200 atoms for the graphitic sheet. Periodic boundary conditions are applied along the x,y, and z directions. For the graphitic phase, a large vacuum region above the graphitic sheets is included. Figure 1 shows the total binding-energy curves obtained by the SCC-DFTB calculations. The binding energy of the zinc blende GaN is -5.91 eV/atom with the nearest-neighbor distance of 1.95 Å, or equivalently the cubic lattice constant of 4.50 Å. The calculated bulk modulus is 195 GPa, in good agreement with the reported LDA result.[23] A considerable amount of electron charge ($0.56\ e$) is transferred from Ga to N, resulting in an ionic bonding nature.[24] The binding energy of the graphitic GaN is -5.55 eV/atom with the nearest-neighbor distance of 1.78 Å, slightly smaller than that of the zinc blende GaN. The energy difference between the zinc blende and graphitic GaN structures of 0.36 eV/atom is about that expected for the rocksalt structure of about 0.5 eV, which is expected to be a stable phase at 50 GPa but not thermodynamically stable under normal conditions.[25–27] This may suggest the possibility of forming graphitic sheets as a metastable phase under some extreme conditions.

We next calculate the strain energy per atom required in order to wrap up a graphitic sheet into a tube, where typical armchair and zigzag GaN nanotubes are shown in Fig. 2. Periodic boundary conditions are applied with vacuum regions (10 Å) between tubes. Strain energies decrease with the increasing diameter of the tube as expected (Fig. 3). We note that in the case of GaN the strain energies are relatively insensitive to the detailed structure of the tubes, in good contrast with the fact that carbon armchair nanotubes are more stable than zigzag nanotubes.[8] Both carbon nanotubes and GaN nanotubes follow classical elasticity theory stating that the strain energy is proportional to the inverse square of the diameter, in good agreement with previous reports.[28–30] The fact that the strain energies of GaN nanotubes are comparable to those of carbon nanotubes ensures a possibility for the synthesis of GaN nanotubes. We also estimate the minimum size of the GaN tubules using Sawada's scheme.[28] It turned out to be (2,2) and (5,0) for the armchair and zigzag GaN nanotube, respectively,[31] comparable to the (5,0) in the carbon tubules.[28]

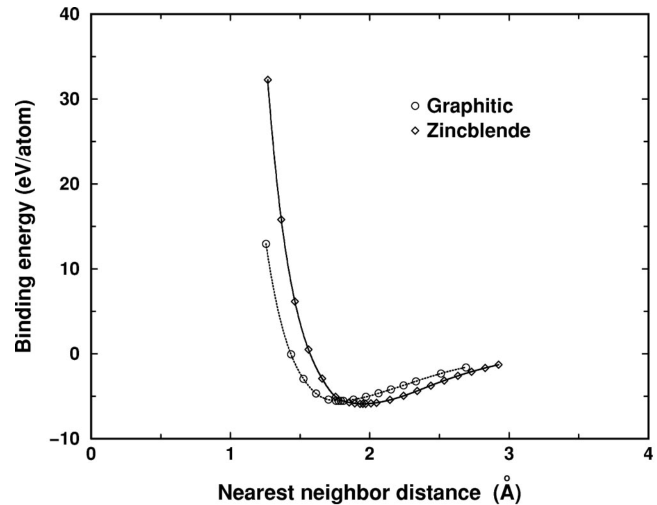


FIG. 1. Total energy curves of cubic and graphitic GaNs as a function of nearest-neighbor distance, calculated by the SCC-DFTB method. The equilibrium distance is 1.95 Å for zinc blende and 1.78 Å in graphitic sheet. The curves are fitted by the cubic-spline method.

Figure 4 shows the band structures and density of states (DOS) of GaN armchair and zigzag nanotubes calculated by the DFT-LDA method. We choose a typical (5,5) armchair nanotube with two layers (20 atoms) and a (9,0) zigzag nanotube with four layers (36 atoms). The respective diameters are 8.47 and 8.81 Å. The band structure for cubic GaN (Ref. 28) shows a direct band gap, in good agreement with the previous first-principles calculations.[23] Graphitic GaN is also a semiconductor with an indirect band gap, in contrast to the metallic characteristics found for graphitic carbon. The details will be described elsewhere.[32] 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

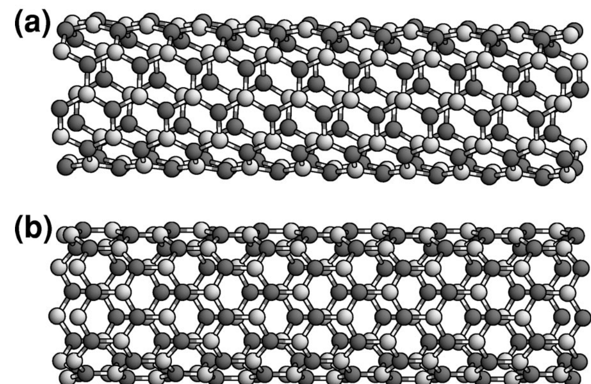


FIG. 2. Typical types of GaN nanotubes (a) (5,5) armchair nanotube, and (b) (9,0) zigzag nanotube. Dark-gray and light-gray spheres indicate Ga and N, respectively.

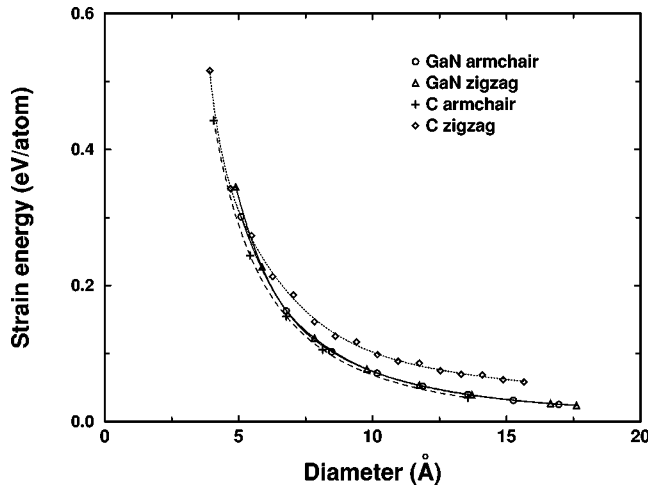


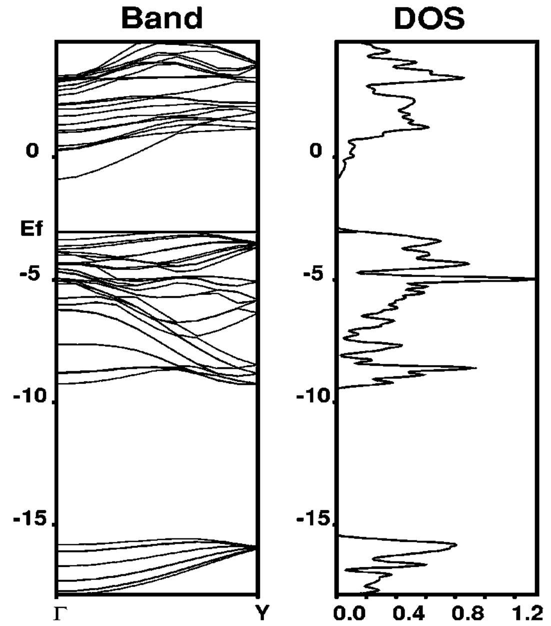
FIG. 3. Strain energies per atom as a function of diameter for GaN armchair and zigzag nanotubes. The strain energies of carbon nanotubes are also shown for comparison (Ref. 7). The curves are fitted by the least-square method.

respective band gaps of (5,5) and (9,0) nanotubes are 2.15 and 2.16 eV.[33] The valence-band maximum of the armchair nanotube is near the middle of the Brillouin zone. The electronic DOSs of nanotubes are similar to each other. More p states are developed by the rehybridization upon wrapping, compared with the graphitic sheet.

In order to investigate the diameter dependence of the band gap, we performed the SCC-DFTB calculations for GaN nanotubes of different diameters. Relaxation resulted in the buckling of 0.06 Å for the (5,5) tube and 0.05 Å for the (9,0) tube, similar to those of BN nanotubes.[34,35] After relaxation, Ga atoms moved toward the tube axis and N atoms moved in the opposite direction, which made the bucking. The buckling was 0.06 Å for the (5,5) tube and 0.05 Å for the (9,0) tube. Comparing to those of BN tubes with similar diameters, the buckings are more significant in BN tubeles.[35] We estimate the convergence of the band-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 band gap of carbon zigzag nanotubes (diamond shape),[32] the band gaps of GaN nanotubes decrease monotonically with decreasing diameter. The band gap of (n,n) GaN nanotubes decreases slightly with decreasing diameter, whereas that of $(n,0)$ GaN nanotubes decreases significantly with decreasing diameter. The band gap converges to the value of the graphitic sheet at large diameter. This decrease of the band gap reflects the ionic bonding character, i.e., s and p bands localized to Ga and N, respectively, are well separated.[36]

Our LDA calculations give a band gap of 2.35 eV for the cubic phase,[33] underestimating the experimental value of 3.52 eV (Ref. 22) by 1.17 eV. The band gap of the graphitic sheet is 2.78 eV. The scissors operation[37,38] gives the corrected band gap of nanotubes at infinite diameter (or equivalently graphitic sheet) of approximately 3.95 eV. We note that band gaps can be tailored by varying the diameter, particularly in zigzag nanotubes.

The key idea in the formation of GaN nanotubes is presumably to use carbon nanotube as a ''template.'' BN nanotubes have been recently synthesized using a carbon nanotube as a nucleation seed, where carbon nanotubes are substituted by the following BN nanotubes.[39] GaN nanotubes may be synthesized similarly at the open edges of carbon nanotubes. Recently, vertically aligned carbon nanotubes have been successfully grown on glass.[40] This aligned carbon nanotube can be a suitable template for GaN nanotube growth. The extra energy costs of forming GaN graphitic sheets can be overcome by GaN adsorption on the existing tubular form of substrates. The precise structures of the GaN



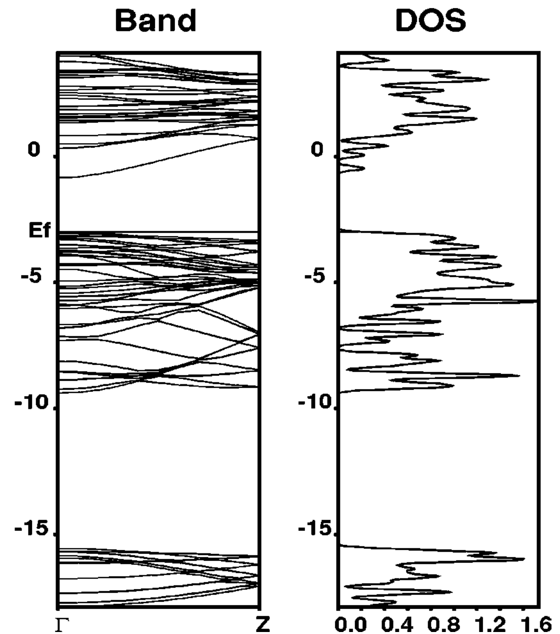


FIG. 4. Band structures along the tube axis and the corresponding density of states of (a) (5,5) GaN armchair nanotube and (b) (9,0) GaN zigzag nanotube. $Y(Z)$ band edge corresponds to the symmetric point $(001/2)2\pi/a$ in the armchair nanotube (zigzag nanotube).

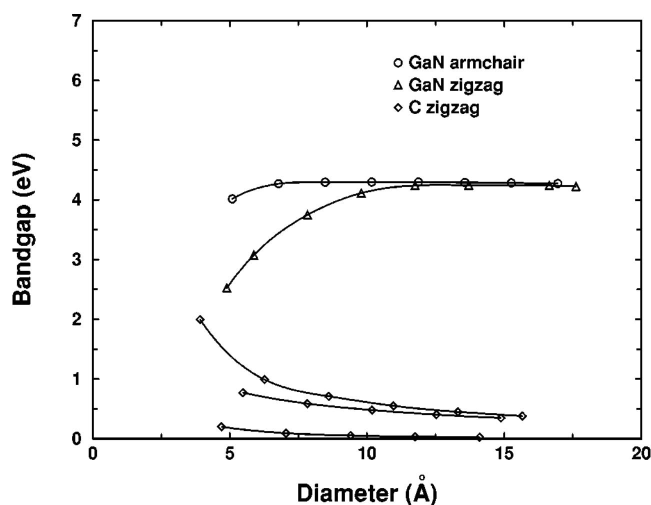


FIG. 5. Band gaps of GaN armchair and zigzag nanotubes as a function of the diameter. The band gaps of carbon zigzag nanotubes (diamond shape) are also shown for comparison. The bottom curve shows the band gap in the case of $n-m=3k$, where k is an integer. Two characteristic band gaps are shown in carbon nanotubes as shown in the next curves.

nucleation on carbon nanotubes is under current investigation.

The strain associated with the lattice mismatch between graphitic GaN and graphite (25%), and the relative energetics of GaN zigzag and armchair nanotubes, will play an important role in the synthesis of GaN nanotubes on carbon nanotubes. We find GaN zigzag nanotubes to be favorable over armchair nanotubes with the strain relaxed within a few GaN layers. Thus metal-semiconductor interfaces can be fabricated. One can also try the arc discharge method with transition metals that anneal away catalytically the edge defects to stabilize the tube growth similar to the carbon nanotubes growth[41] and BCN nanotubes growth.[42] This opens the possibility for this structure to be applied for ultimate nanoscale photodetectors or electroluminescent devices.

In summary, we have performed density-functional calculations to search for the stability and electronic structures of GaN nanotubes. Our calculations suggest the possibility of synthesis of a GaN nanotube under some experimental conditions. The band gap decreases with the decreasing diameter. 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 the cubic GaN phase. This strongly suggests that ultimate nanoscale optoelectronic devices for full color displays may be realized with sophisticated modern synthesis techniques.

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