GAN NANOTUBES

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ABSTRACT
We perform parametrized density-functional calculations to predict the stability and formation mechanism of GaN nanotubes. Strain energies of GaN nanotubes are comparable to those of carbon nanotubes, suggesting the possibility for the formation of GaN nanotubes. We note that an intermediate phase with [4,6,10] polygons exist at armchair tube edge, which may play as a nucleation seed of further tube growth.

INTRODUCTION
Carbon nanotubes (C-nTs) 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, researchers on carbon nanotubes have been activated. The physical properties of carbon nanotubes as denoted *(n,m)* are correlated with their diverse phases. Armchair *(n,n)* carbon nanotubes are metallic [5,6], while zigzag *(n,0)* C-nTs are semiconductors with a finite band gap except the case of $n - m = 3k$ (k: integer) which is a small band gap semiconductor [7]. Band gap can be controlled by varying the diameter, thus allowing band gap engineering [5, 8]. Strong electron field emission from C-nTs have been observed, suggesting the applicability to flat panel displays [9, 10]. Despite such efforts, applications of C-nTs to memory devices and quantum transport devices are still challenging.

With an advent of epitaxial growth techniques for GaN, efficient blue light-emitting diodes have been realized, promising its application to full color display [11]. Although $In_xGa_{1-x}N$ has been tried for band gap engineering by varying In composition, it is still difficult to grow and control high In composition 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 (nT), using parametrized density functional (DF) calculations. We will show that GaN nTs are as stable as carbon nTs and can be synthesized under some extreme conditions. Pure boron-nitride and boron-carbon-nitride nTs have been successfully produced by arc discharge [13, 14]. The existence of BN-nTs suggests the possibility of other nitride nT synthesis such as CN and GaN. The present calculations show that the strain energies, the energy costs to wrap up graphitic GaN sheets into nTs, are comparable with those of carbon nTs, ensuring again the possibility of GaN nT formation. Yet,

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the initial nucleation seeds for GaN nT formation will play a crucial role for growth. We find that an intermediate phase which is composed of [4,6,10] polygons may play as a nucleation seed during the growth.

THEORETICAL APPROACHES

We adopt in this work self-consistent charge density-functional-based tight-binding (SCC-DFTB) approach. The SCC-DFTB method uses a basis of numerically obtained *s*, *p*, and *d* atomic orbitals. Hamiltonian overlap matrix elements are evaluated by 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. They decay as 1/r and thus account for the Madelung energy of the system. Further details of the SCC-DFTB method have been published elsewhere [15].

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 can be stabilized on various cubic substrates [16, 17]. We first calculate the total binding energies of ZB and graphitic phases of GaN using SCC-DFTB method in order to study the relative stabilities. We choose a cubic supercell of 216 atoms for ZB 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 between graphitic sheets is included. Figure 1 shows total binding-energy curves obtained by the SCC-DFTB calculations. The binding energy of the ZB GaN is -5.91 eV/atom with the nearest neighbor distance of 1.950 Å, or equivalently the cubic lattice constant of 4.503 Å. The calculated bulk modulus is 195 GPa, in good agreement with the reported local-density-approximation results [18]. A considerable amount of electron charge (0.56 e) is transferred from Ga atom to N atom, resulting in an ionic bonding nature. The binding energy of the graphitic GaN is -5.55 eV/atom with the nearest neighbor distance of 1.775 Å, smaller than that of the ZB GaN. This difference in the binding energy suggests the graphitic GaN to be energetically unfavorable over the ZB or the wurtzite GaN. Yet this small magnitude of the energy difference opens the possibility of forming graphitic sheets as a metastable phase.

We next calculate the strain energy per atom required in order to wrap up a graphitic sheet into a tube. Periodic boundary conditions are applied with vacuum regions (10 Å) between tubes. Strain energies decrease with increasing the tube diameter as expected (Fig. 2). We note that strain energies of GaN nanotubes are relatively insensitive to the detailed structures, in good contrast with the fact that armchair carbon nTs are more stable than zigzag carbon nTs [8]. The transferred charges are localized in p_z orbitals of N sites [19]. The circumferential N-N distances in GaN armchair and zigzag nTs are 2.66 and 3.07 Å, respectively, much larger than the C-C distances in C-nTs (1.42 and 1.23 Å). This gives relatively less rehybridization and less bond-bending, making the strain energies in GaN nTs insensitive to the detailed structures of tubes. Both C-nTs and GaN nTs follow classical elasticity theory stating that the strain energy is proportional to the inverse square of the tube diameter. The fact that the strain energies of GaN nTs are comparable to those of C-nTs ensures a possibility for the synthesis of GaN nTs.

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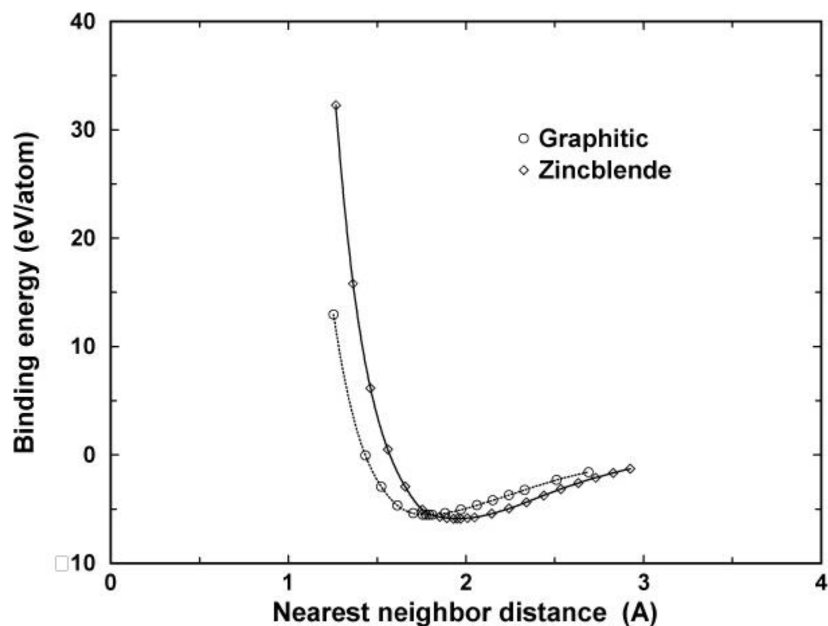

Figure 1. Total energy curves of cubic and graphitic GaNs as a function of nearest neighbor distance, calculated by SCC-DFTB method. The equilibrium distance is 1.95 Å for zincblende and 1.775 Å in graphitic sheet. The curves are fitted by the cubic-spline method.

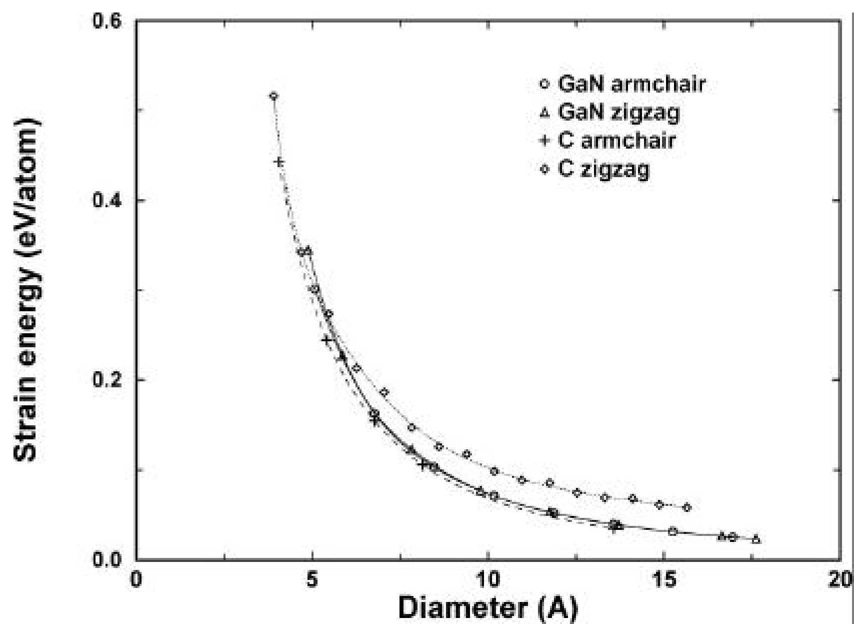

Figure 2. Strain energies as a function of diameter for armchair and zigzag GaN nanotubes. The strain energies of carbon nanotubes are also shown for comparison [8]. The curves are fitted by the least-square method.

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The stability and long tube formation strongly depend on the edge structures. For armchair tubes, the Ga-N pairs are formed, as shown in Fig. 3(a). For the edge energy calculations we choose (5,5) nanotube with a vacuum region of 10 Å. Both open edges with three more layers from the edges are fully relaxed by the steepest decent relaxation scheme. The edge Ga-N pairs are stabilized by forming asymmetric dimers with a dimer bond length of 1.58 Å, shorter than the surface bond length of 1.78 Å, and an asymmetry of 0.23 Å. The N atoms where charges are accumulated, form up-atoms and occupied states. This buckling is similar to that of asymmetric dimerizations on Si(100) surfaces [20]. For zigzag tubes we choose (9,0) nanotube which has similar diameter to (5,5) nanotubes. Zigzag edge has either Ga-terminated or N-terminated edges. The Ga-terminated and the N-terminated edges on both sides of the edges are chosen in order to keep the stoicheometry in the calculations. The edges are then fully relaxed similarly to the armchair tubes. The Ga-terminated surface states are degenerate at Fermi level. Full relaxation of this edge results in symmetry-breaking and two Ga-N pairs are formed, as shown in Fig. 3(b). The N-terminated edges are stable with shorter bond lengths of 1.69 Å, compared with a surface bond of 1.78 Å (Fig. 3(c)). The edge energy of armchair and zigzag tube is 2.82 and 4.32 eV/Ga-N pair, respectively, suggesting that the armchair edge is more stable than the zigzag edge.

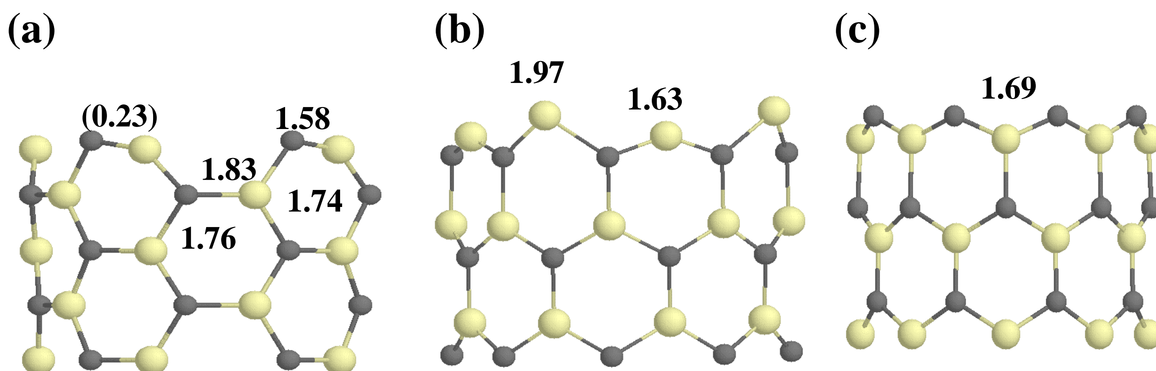

Figure 3. Atomic geometries of GaN nanotube edges for (a) armchair edge, (b) Ga-terminated zigzag edge and (c) N-terminated zigzag edges. Lighter and darker atoms represent Ga and N respectively. The values in parenthesis is the asymmetry. All units are in Å.

We find an intermediate phase of armchair edges which is formed during the molecular dynamics simulations at high temperature [19], as shown in Fig. 4. Instead of forming buckling at armchair edge, the edges form [4,6,10] polygons where the Ga-N bonds at edges are 1.69 and 1.88 Å at hexagon and square edges, respectively. Weak bonds are formed with bond lengths of 1.99 Å between the edge atoms and the second layer atoms. These weak bonds play an important role in the fragmentation process [19]. The energy difference from fully relaxed (5,5) nanotube is 0.37 eV per GaN edge pair. This intermediate phase is in fact similar to that of BN nanotube edges [21]. Depositing Ga-N pair to the square at edge will generate a complete hexagon, suggesting that [4,6,10] polygons may play as a nucleation seed during the growth of the GaN nanotubes.

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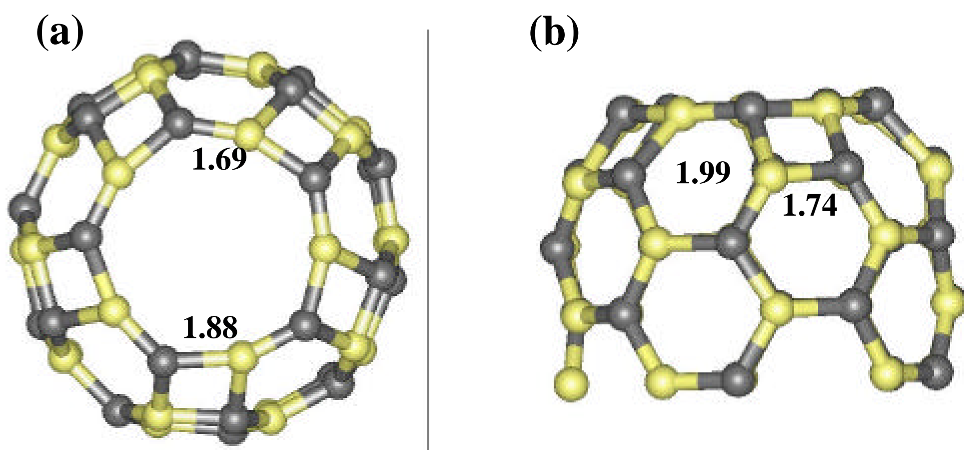

Figure 4. (a) Top and (b) side views of an intermediate phase of (5,5) GaN nanotube. Brighter and darker atoms represent Ga and N atoms, respectively. All units are in Å.

Stability of the edge can also be examined by the frustration energy, *i.e.*, the energy required to have a bond-switching at the edge. With a single bond-switching at armchair tube edge, one N-N and one Ga-Ga bonds are generated, as shown in Fig. 5. The N-N bond is stable with a bond length of 1.45 Å, whereas the Ga-Ga bond is repulsive. This is understandable due to the charge transfers from Ga atom to N atom, resulting in less screening for Ga ion-ion repulsive interactions. The energy increased by 1.58 eV. The frustration at Ga-terminated edge creates one N-N bond and two Ga-Ga bonds, requiring an extra energy cost of 3.22 eV. On the other hand, the frustration at N-terminated edge generates two N-N bonds and one Ga-Ga bond. This requires only 0.02 eV. This small energy cost originates from the energy gain by forming two N-N bonds. This suggests that frustration effect may dominate the front growing edges in case of N-terminated edge of zigzag nanotubes and tubes may not grow further. Catalytic growth similar to the single-wall carbon nanotubes [2, 14] may be necessary to have a long tube growth at zigzag GaN nanotubes.

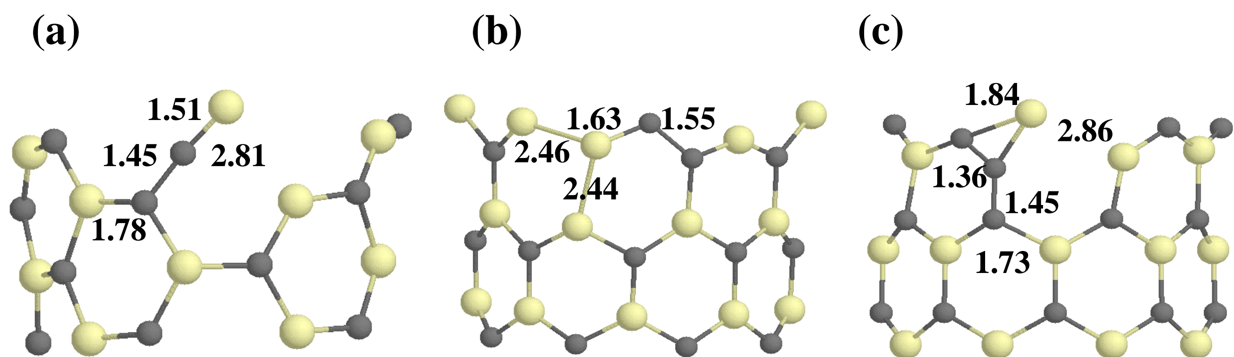

Figure 5. Frustrated edge structures of (a) (5,5) armchair edge, (b) Ga-terminated zigzag edge and (c) N-terminated zigzag edge. Brighter and darker atoms represent Ga and N atoms, respectively. All units are in Å.

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CONCLUSION

In summary, we have performed density-functional based tight-binding total energy calculations to search for the stability and formation mechanism of GaN nTs. The calculations for the strain energy reveal that GaN nTs are as stable as C-nTs and can be formed at some extreme conditions. The armchair edge is stable and an intermediate phase with [4,6,10] polygons may play as a nucleation seed for a long tube growth.

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