Chiral tubules of hexagonal BC₂N

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We propose a family of nanotubules originating from a hexagonal BC_2N sheet. Because of the anisotropic structure of the BC_2N sheet, there are a variety of ways to obtain chiral structures by rolling the BC_2N sheets into tubules. We performed first-principles and tight-binding band-structure calculations and predict that the chiral BC_2N tubules will behave as semiconductors that can be doped with either acceptors or donors. Since the BC_2N sheets have anisotropic conductivity in the in-plane directions, helical currents are expected for the chiral tubules. The tubules will resemble nanoscale coils.

The discovery of carbon tubules[1] has triggered scientific interest about their structural, mechanical, and electronic properties. Theoretical studies[2,3] show that either metallic or semiconducting tubules are obtained depending on the radii and chiralities of tubules. The structures of tubules can be uniquely classified using a notation (n,m) proposed by Hamada *et al.*:[2] The (n,m) tubule is obtained by rolling a graphite sheet so that one hexagon will connect another one separated by $nA_1 + mA_2$; here A_1 and A_2 are primitive translation vectors of the graphite sheet. The character of the electronic structures of (n,m) tubules can be qualitatively derived from that of the graphite sheet with each C atom having sp^2 orbital hybridization plus a p_z orbital forming the π states. However, the C-bond angles deviate from the ideal 120° on the tubule's wall resulting in an increase of the π^*-σ^* orbital hybridization. This hybridization has been found to lower the π^* band below the Fermi level (E_F) in cases of small-diameter carbon tubules according to first-principles calculations.[4] This result was not predicted from previous tight-binding (TB) calculations.[2,3]

Recently, hexagonal BN has been proposed as an interesting class of tubules.[5] The electronic structures of BN tubules have been studied using the TB scheme, and large gap semiconducting behavior was predicted. First-principles total-energy calculations within a framework of the local density approximation (LDA) have also been done[6] for BN tubules and buckling of the B-N bonds was found to lower the structural energies. This buckling moves N atoms outward and keeps the bond angle of B atoms at 120°. In this LDA calculation, the total-energy increases and decreases upon rolling, respectively, BN sheets and strips into tubules have been estimated. The increases have been found to be less than those in the case of graphite, while the decreases have been found to be larger. It is therefore concluded at least energetically that BN tubules may be more likely to form than graphite tubules. Another interest in this system is the possibility of C impurities on substitutional sites resulting in either electron or hole carriers in the BN tubules.

Here we consider another class of the tubules based on graphitic compounds consisting of B, C, and N. These system are expected to have stabilities intermediate between those of graphite and BN tubules. Specifically, we propose tubules originating from hexagonal BC_2N sheets. Due to the

anisotropic geometry of hexagonal BC_2N sheet, there are different ways of rolling the sheet into chiral tubules compared to graphite and BN sheets. In contrast to graphite and BN sheets, the anisotropy of BC_2N sheets results in an anisotropic conductivity in the in-plane directions. When chiral BC_2N tubules are formed, the most conducting directions of the original sheets make chiral trajectories so helical currents can result for these tubules. Chiral BC_2N tubules are thus expected to be nanoscale coils. In the following, we explain the details of BC_2N-tubule structures and give some of the results of our electronic structure calculations.

First we discuss possible atomic structures of hexagonal BC_2N sheets, which were previously investigated using first-principles total-energy calculations.[7] Experimentally, it is known that a honeycomb structure exists for BC_2N sheet but the exact atomic configurations have not been determined.[8] Possible atomic configurations have been investigated and the geometries shown in Figs. 1(a) and 1(b) were found to be the most stable geometries among several candidates.[7] [The most stable geometry is shown in Fig. 1(b) with total energy lower than that of Fig. 1(a) by 0.13 eV/atom.] In both geometries, covalent bond lenghs are set to be common: $d_{C-C}=1.42$ Å, $d_{B-C}=1.55$ Å, $d_{B-N}=1.45$ Å, and $d_{C-N}=1.32$ Å. In the geometry of Fig. 1(a) all bond angles are 120°, while in the geometry of Fig. 1(b) the angles deviate from 120° by as much as $\pm 2°$. The calculated electronic structures of geometries in Figs. 1(a) and 1(b) are metallic and semiconducting, respectively. Hereafter, we refer to the hexagonal BC_2N sheets of Figs. 1(a) and 1(b) as type-I and type-II sheets, respectively, in the same manner as Ref. 7.

If we consider tubule structures obtained by rolling either the type-I or type-II sheets in a manner similar to graphite tubules, the series can be classified by the notation of Hamada *et al.*[2] Contrary to the cases for graphite and hexagonal BN, a unit cell here consists of eight atoms, i.e., four C atoms and two B and two N atoms. Although the primitive unit cell of the type-II sheet is half that of the type-I sheet, we use common lattice vectors. A series of lattice indices is indicated in Figs. 1(a) and 1(b), which uniquely determines the way to roll these sheets into tubules. Since we use common lattice vectors, half integers are used for indices on the type-II sheet. Figures 2(a) and 2(b) show examples of (n,n)
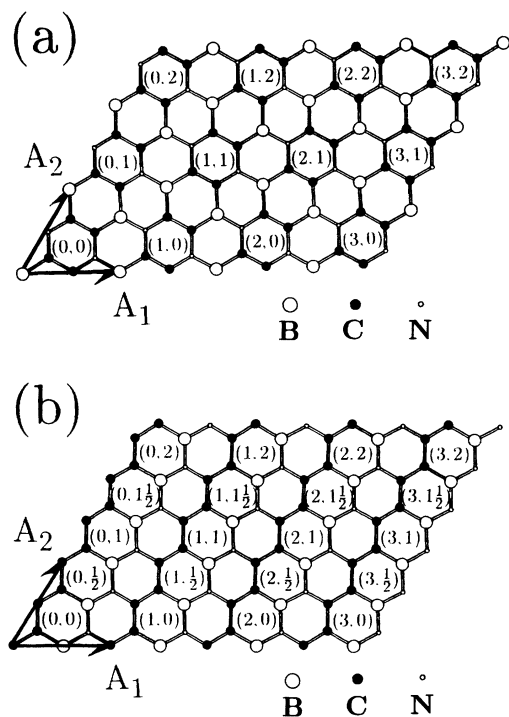
FIG. 1. Atomic configurations of (a) type-I sheet and (b) type-II sheet of hexagonal BC$_2$N. Primitive vectors A_1 and A_2 are also indicated. Solid cricles denote C atoms while large and small open circles denote N atoms and B atoms, respectively. A series of lattice indices is indicated at the center of each unit cell. Since the unit cell of the type-II sheet is half that of the type-I sheet, half integers are used on the type-II sheet.

FIG. 2. The BC$_2$N (4,4) tubules obtained by rolling (a) type-I sheets and (b) type-II sheets. The vertical direction is parallel to the tubule axes. Some atoms in the back sides are not shown to avoid complexity. The chiral alignments of C, B, and N atoms are seen in these structures.

($n=4$) tubules of the type-I sheet and the type-II sheet, respectively. [Note that a diameter of a BC$_2$N (n,m) tubule is almost twice that of the graphite (n,m) tubule.] The honeycomb pattern on the tubule surface does not have chirality, while B, C, and N atoms make chiral alignments in each tubule. The series of (n,n) tubules thus has chirality in atomic alignment. From Figs. 1(a) and 1(b), one can notice that the ($n,0$) tubules also have chirality in the atomic alignment even though the surface honeycomb patterns are non-chiral. Hexagonal BC$_2$N sheets thus have many ways to form chiral tubules compared to the graphite and BN sheets.[9] This is due to the anisotropic structure of BC$_2$N sheets. We will refer to (n,m) tubules originating from type-I sheets and type-II sheets as type-I (n,m) tubules and type-II (n,m) tubules, respectively.

Electronic band structures for the chiral BC$_2$N tubules are shown in Figs. 3 and 4. We have performed LDA calculations using a plane-wave basis set with a cutoff energy 36 Ry and pseudopotentials obtained using the Kleinman-Bylander scheme.[10] Other conditions for this calculation are the same as those of Ref. 4. We find that the present calculations reproduce the band structures and the relative total energies of the type-I and type-II sheets obtained using localized-orbital basis sets.[7] We have perfomed total-energy and band-structure calculations of the type-I (2,2) tubule and the type-II (2,2) tubule assuming that all atomic coordinates on
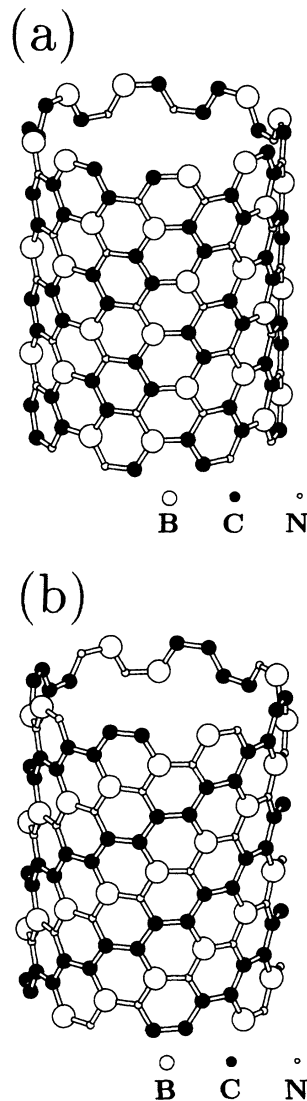
these tubules are obtained by rolling the sheets so that all bond lengths are kept the same as those in BC$_2$N sheets. According to the present calculation, metallic and semiconducting band structures for the type-I (2,2) tubule and the type-II (2,2) tubule are found, respectively. From an analogy to the electronic structures of the graphite (n,m) tubules,[2,3] we believe that type-I (n,m) tubules can be either metals or semiconductors depending on their radii and chiralities. On the other hand, type-II (n,m) tubules are expected to be semiconducting independent of the (n,m) configuration similar to the BN (n,m) tubules. Within the present geometrical assumption, the calculated total-energy of the type-II (2,2) tubule is lower than that of the type-I (2,2) tubule by 0.28 eV/atom. Since both sets of atomic coordinates have not been fully optimized to total-energy minimized geometries, the calculated energy difference is inaccu-
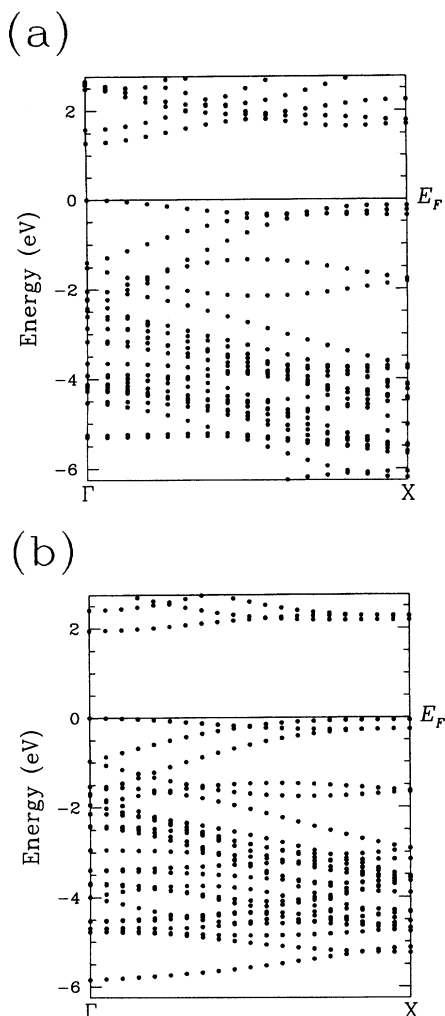
(a)

(b)

FIG. 3. Energy band structures of type-II (2,2) tubules obtained by (a) LDA calculations and (b) sp^3s^* nearest-neighbor TB calculations.
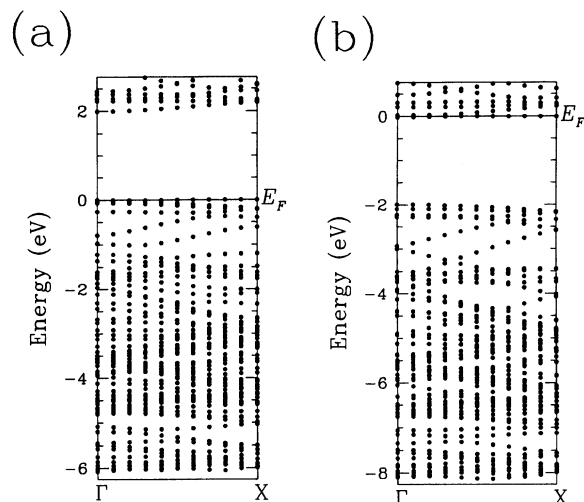
(a)　　　　　　(b)

FIG. 4. Energy band structures of the type-II (2,2) tubules having an impurity C atom (a) on a N site and (b) on a B site obtained by the sp^3s^* nearest-neighbor TB calculation. The locations of E_F here correspond to the locations of the impurity-induced levels. The assumed periodic boundaries are twice as those of the (2,2) tubules so the first Brillouin zones are half of those in Fig. 3.

rate. However, we believe that the type-II (2,2) tubule is more stable than the type-I (2,2) tubule since the calculated total energy of the original type-II sheet shows remarkable stability compared to that of the type-I sheet. Similar stability was also found in a previous calculation.[7] The origin of the stability of the type-II sheet and type-II tubules is associated with the maximized number of C-C and B-N bonds, which are the strongest chemical bonds among those of B, C, and N atoms. Although total-energy calculations for different types of tubules have not been done, we expect that the type-II (n,m) tubules should be found dominant in experimental samples. The growth mechanisms of tubules is still an open question; however, the formation of type-II (n,m) tubules could be determined by local chemical conditions which prefer strong C-C and B-N bonds.

A calculated band structure of the type-II (2,2) tubule is shown in Fig. 3(a). A direct band gap of 1.28 eV is seen at the Γ point, which is smaller than the band gap of the type-II sheet of 1.76 eV. Although each B-N bond on the wall of the BC_2N tubule is expected to buckle according to the results of the BN tubules,[6] we believe that the resulting band structure

will be essentially unchanged. This belief is based on the results of the calculation of BN tubules:[6] The calculated band structures of BN tubules were found to be relatively insensitive to the buckling of the B-N bonds.

The calculated band gap is typical of conventional semiconductors. We have also examined whether shallow levels are formed upon doping the type-II tubules with impurities. Although there are many ways to dope the BC_2N tubules, here we focus on a C impurity which sits on either a B site or a N site of the tubules. Within the framework of the band-structure calculation, a large unit cell is necessary to avoid artificial dispersion of an impurity-induced state. We have chosen the TB scheme for the large-cell calculation with sp^3s^* nearest-neighbor TB parameters[11] so that these parameters reproduce the LDA results of the type-II sheet in a region near E_F. We then apply the parameters to tubules. Figure 3(b) shows the band structure of the type-II (2,2) tubule obtained by the present TB calculation. Although there is a discrepancy between the results of the LDA and the TB calculations in the details of the band dispersion and the band gap, the main features agree for states near the valence-band maximum and the conduction-band minimum. For studying the impurity-induced level, a TB calculation of the type-II (2,2) tubule has been performed using a cell size twice as large as the original one. Figures 4(a) and 4(b) show band structures of the type-II (2,2) tubules having a substitutional C impurity atom on a N site and a B site, respectively. Despite the use of periodic boundary conditions, the impurity-induced levels show small energy dispersions indicating that these calculations describe a picture of localized impurity states. The band structure of Fig. 4(a) shows the existence of an acceptorlike level located 0.03 eV above the valence-band top while that of Fig. 4(b) shows the existence of a donorlike level located 0.03 eV below the conduction-

band bottom. Although the present calculation gives only an estimate of these impurity levels, we can say at least that the C impurities do not form very deep levels in the energy gap. This shallow level may appear in other (n,m) tubules. As for the hexagonal BC$_2$N sheet, the resistivity was measured at various temperatures,[8] and a thermal gap of 0.03 eV was obtained indicating the existence of shallow levels. We believe that the experimental results also imply the possibility of the doped BC$_2$N tubules.

In summary, we have exhibited the atomic and electronic structures of BC$_2$N tubules. Due to the anisotropic geometry of the BC$_2$N sheet, chiral structures are expected to be dominant. Possible chiral tubules have been found to be semiconducting, and we suggest that either p-type or n-type semiconductors could be obtained by controlling the atomic stoichiometry of the sample. For example, a composition of B$_{1-\delta}$C$_{2+\delta}$N gives C impurities on B sites resulting in electron carriers while another composition of BC$_{2+\delta}$N$_{1-\delta}$ gives C impurities on N sites resulting in hole carriers. Since the original sheets have anisotropic conductivity in the in-plane directions, both p-type and n-type chiral tubules could be helical conductors. An interesting question is whether they behave like nanoscale coils. When metal atoms with magnetic moment are put inside the chiral tubules using capillarity effect,[12] it will also be interesting to examine whether the current of chiral tubules plays some role in causing magnetic ordering of the metal atoms. Some new theoretical formulations may be useful for describing helical currents in the tubules. For example, we may consider a helical momentum operator defined as a linear combination of the operators of translational momentum along a tubule's axis and the angular momentum around a tubule's circumference, which is uniquely determined by defining a chiral angle of the current. (A similar idea has already appeared in describing the electronic eigenstates in the chiral graphite tubules.[13]) A remaining problem is how to treat scattering processes for the carriers in tubules. These should not be the same as those for the case of a one-dimensional conductor. We hope that experimental studies of the possibility of formation of the BC$_2$N tubules and their conductivities will be motivated by our predictions.

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