Are fluorinated BN nanotubes \( n \)-type semiconductors?

H. J. Xiang,1, 2 Jinlong Yang,1, 2 J. G. Hou,1, 2 and Qingshi Zhu1, 2

1Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, Anhui 230026, People’s Republic of China
2USTC Shanghai Institute for Advanced Studies, University of Science and Technology of China, Shanghai 201315, People’s Republic of China

The structural and electronic properties of fluorine (F)-doped BN nanotubes (BNNTs) are studied using density functional methods. Our results indicate that F atoms prefer to substitute N atoms, resulting in substantial changes of BN layers. However, F substitutional doping results in no shallow impurity states. The adsorption of F atoms on B sites is more stable than that on N sites. BNNTs with adsorbed F atoms are \( p \)-type semiconductors, suggesting the electronic conduction in F-doped multiewall BNNTs with large conductivity observed experimentally might be of \( p \)-type due to the adsorbed F atoms, but not \( n \)-type as supposed before.

Pure boron nitride nanotubes (BNNTs) are semiconductors regardless of diameter, chirality, or the number of walls of the tubes. This contrasts markedly with the heterogeneity of electronic properties of carbon nanotubes, and also makes BNNTs particularly useful for potential nanoelectronic applications. From the applications viewpoint, obtaining \( n \)-type and/or \( p \)-type semiconducting BNNTs is very important for the use in the nanoscale electronic device, such as the \( n \)-type as supposed before. However, the behavior of dopants in semiconductors is often far from trivial. Then does F-doping really induce \( n \)-type conduction in BNNTs?

In this Letter, we conduct a first-principles study on F-doped BNNTs to address this issue. Both adsorption and substitution of F on BNNTs are examined. Surprisingly, neither adsorption or substitution of F on BNNTs results in \( n \)-type semiconductors, contrasting sharply to previous supposition. Our calculations are performed using the local density approximation in the density functional theory as implemented in VASP. The electron-ion interaction is described by ultrasoft pseudopotentials and the cut-off energy is set to 347.9 eV.

We mainly focus on a typical zig-zag BNNT, i.e., BN(10,0) nanotube. Test calculations indicate that the doping behavior for BN(5,5) NT and BN two dimensional sheet (a model for nanotube with radius \( R = \infty \)) is qualitatively the same as that for BN(10,0) nanotube. Our supercell for BN(10,0) nanotube contains 80 atoms. First from the optimized structure of the pure BN(10,0) nanotube, we substitute one B or N with one F atom (abbreviated as \( S_F^B \) and \( S_F^N \) respectively). Both relaxed structures are shown in Fig. (a) and (b) respectively. In both cases, F substitution induces significant deformation of the BN layer. Since F is usually in \(-1\) valence state, F is bonded with only one adjacent B or N atom along the axis direction. A remarkable difference between the two structures is that F atom doesn’t lie in the BN layer and the other two B atoms with dangling bonds come close to each other to form a homo elemental bond in \( S_F^N \). Another difference is that the cross section of the tube in \( S_F^N \) is no longer a perfect circle as the B atom bonded with F comes out from the BN plane. To see which substitution is more favorable, we compare the defect formation energy in these two cases. The formation energy is defined as: 

\[
E_{\text{form}} = E_{\text{tot}} - n_B \mu_B - n_N \mu_N - n_F \mu_F,
\]

where \( E_{\text{tot}} \) is the total energy of the system, \( n_B, n_N, \) and \( n_F \) are the number of B, N, and F atoms respectively, and \( \mu \) is the chemical potential. \( \mu_B \) and \( \mu_N \) depend on the growth condition: In the N-rich environment, \( \mu_N \) (−8.629 eV) is obtained from nitrogen in the gas phase, while a metallic \( \alpha \)-B phase is used as the reservoir for the B-rich environment (−7.491 eV for \( \mu_B \)). In both cases, \( \mu_B \) and \( \mu_N \) are linked by the thermodynamic constraint: 

\[
\mu_B + \mu_N = \mu_{\text{BN}}^{\text{tubep}},
\]

where \( \mu_{\text{BN}}^{\text{tubep}} \) is the chemical potential per BN pair in the pristine BN nanotube. Since both systems has one F atom, the value of \( \mu_F \) makes no difference to the difference of the formation energy. So, we don’t specify \( \mu_F \) explicitly. The calculated formation energies are shown in Table I. The formation energy difference between \( S_F^B \) and \( S_F^N \) is 9.778 (3.707) eV in the B (N) rich environment, suggesting F strongly prefers to substitute N in BNNTs. This is not surprising since the large electronegativity of F will result in stronger F-B bond. The homo elemental bond in \( S_F^N \) partially saturates the dangling bonds of B atoms, also contributing the stability of \( S_F^N \).
The band structure of $S_F^N$ is shown in Fig. 2. For better comparison, the band structure of the pristine BN(10,0) nanotube with the same supercell is also plotted in Fig. 2. We can see both pristine and F-doped BN(10,0) nanotubes are semiconducting with a band gap of 3.9 and 3.2 eV respectively. Density of states (DOS) analysis shows that the bands related to F 2p states mainly lie in $-4 \text{ to } -8$ eV with respect to the valence top. F substitutional doping induces an unoccupied localized state in the gap, which is mainly contributed by the two B atoms connected with the homoelemental bond as shown in the inset of Fig. 2(b). However, this state is neither a shallow acceptor state nor a shallow donor state. So we don’t expect such F substitutional doping will result in large increase of electrical conductivity.

To elucidate the origin of the drastic increase in the conductivity of F-doped BNNTs, the adsorption of F on BN(10,0) nanotube is examined. We find that one F atom prefers to adsorb on the B site (labeled as $A^B_F$, as shown in Fig. 1(c)), since the adsorption of F on N site is unstable and the F atom will eventually adsorb on the B site. The electronic band structure for $A^B_F$ is shown in Fig. 2(c). Clearly, the system displays a degenerated $p$-type semiconducting behavior. There are two bands with similar character crossing the Fermi level. Both states are rather delocalized as can be seen from the local DOS of one of the bands (shown in the inset of Fig. 2(c)). So only 1.25% F adsorption on BNNTs will lead to drastic increase in conductivity.

Besides the doping behavior of one F atom, we also study the BN(10,0) nanotube doped with two F atoms. First, adsorption of two F atoms is examined. We find that the configuration (as shown in Fig. 2(a)) where both F atoms adsorb on two B sites is favourable over the one where the second impurity atom adsorbs on the adjacent N site. This differs fundamentally the adsorption of H atoms on BNNTs.[11] Electronic structure calculations on this configuration indicate that it is a degenerated $p$-type semiconductor with larger DOS in the Fermi level than $A^B_F$, as shown in Fig. 2(d). Then BN(10,0) nanotube with two substitutional F atoms as shown in Fig. 2(b) is studied. The DOS of this configuration is shown in Fig. 2(c), indicating that BN(10,0) nanotube with two substitutional F atoms has similar semiconducting properties as $S_F^N$. Finally, BN(10,0) nanotubes with one substitutional F atom and one adsorbed F atom are investigated. The most stable configuration is the structure shown in Fig. 2(c), where the excess F atom is bonded with one of the two B atoms which form the homoelemental B-B bond in $S_F^N$. The DOS of this configuration is shown in Fig. 2(f), indicating that there is a half occupied localized state due to the unsaturated B dangling bond at approximately 1.4 eV above the valence top. Thus we don’t expect this configuration will have high electric conductivity since there is no shallow impurity related states. Besides the most stable configuration, we also consider other metastable configurations where one more F atom adsorbs on other B sites in $S_F^N$. All these metastable structures are found to be $p$-type semiconductors as $A^B_F$.

Based on our calculations, we suggest that the experimentally observed three orders decrease in resistivity of F-doped BNNTs might be due to F adsorption instead of F substitution. One may concern the stability of the adsorption of F atoms on BNNTs since experimental studies indicated that the doped fluorine escapes easily when the tube is exposed to air or under standard beam irradiation in the electron microscope. Our results indicate that the adsorption of F on BNNTs is as easy as the substitution of F in BNNTs as compared to F adsorption on BNNTs in the N rich environment, and the formation of $A^B_F$ is much easier than that of $S_F^N$ in the N rich environment, as can be seen from their formation energies. Our nudged elastic band (NEB) calculations indeed show that the F dissociation in single-walled BNNTs with adsorption of F atoms is easier than that in $S_F^N$ (with dissociation energy 3.44 eV and 5.86 eV for $A^B_F$ and $S_F^N$ respectively). However, Tang et al. synthesized F-doped BNNTs through the introduction of F atoms at the stage of multiwalled nanotube growth[8] instead of doping F after the stage of BNNTs growth. We suppose that F adsorption occurs in the stage of BNNTs growth, the F adsorbed on the inner walls of the multiwalled BNNTs should be stable. However, our calculations don’t exclude the possibility of F substitution: F substitutional doping might also occur along with F adsorption, especially in the B rich environment. In fact, F substitutional doping destroys the six-numbered BN atomic ring, which is in accord with experimental findings.[8]

To summarize, first-principles calculations have been performed to study the structural and electronic properties of fluorinated BNNTs. F atoms prefer to substitute N atoms, resulting in substantial structural changes of the BN layers but little change in conductivity. The adsorption of F on B sites is more favourable than that on N sites due to the large electronegativity of F. BNNTs with adsorbed F atoms are $p$-type semiconductors with enhanced conductivity than the pristine nanotubes. Our results clearly demonstrate that F-doped multilayered BNNTs synthesized experimentally are the most likely $p$-type semiconductors. The present study also suggests that care should be taken when predicting from intuition doped semiconductors’ electronic properties. Further experimental studies on F-doped BNNTs are awaited to confirm our results.

This work is partially supported by the National Project for the Development of Key Fundamental Sciences in China (G1999075305), by the National Natural Science Foundation of China (50121202, 10474087), by the USTC-HP HPC project, by the EDF of USTC-SIAS, and by the SCCAS.
Corresponding author. E-mail: jlyang@ustc.edu.cn

[1] A. Rubio, J. L. Corkill, and M. L. Cohen, Phys. Rev. B 49, R5081 (1994);
[2] N. G. Chopra, R. J. Luyken, K. Cherrey, V. H. Crespi, M. L. Cohen, S. G. Louie, and A. Zettl, Science 28, 335 (1994); A. Loiseau, F. Willaime, N. Demoncy, G. Hug, and H. Pascard, Phys. Rev. Lett. 76, 4737 (1996).
[3] X. J. Wu, J. L. Yang, J. G. Hou, and Q. S. Zhu, Phys. Rev. B 69, 153411 (2004).
[4] K. Suenaga, C. Colliex, N. Demoncy, A. Loiseau, H. Pascard, and F. Willaime, Science 278, 653 (1997); W. Mickelson, S. Aloni, W. Q. Han, J. Cumings, and A. Zettl, ibid 300, 467 (2003).
[5] C. Tang, Y. Bando, Y. Huang, S. Yue, C. Gu, F. Xu, and D. Golberg, J. Am. Chem. Soc. 127, 6552 (2005).
[6] S. Limpijumnong, S. B. Zhang, S. H. Wei, and C. H. Park, Phys. Rev. Lett. 92, 155504 (2004).
[7] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. 45, 566 (1980); J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).
[8] G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993).
[9] D. Vanderbilt, Phys. Rev. B 41, 7892 (1990).
[10] X. J. Wu, J. L. Yang, J. G. Hou, and Q. S. Zhu, J. Chem. Phys. 121, 8481 (2004).
[11] G. Mills, H. Jonsson, and G. K. Schenter, Surface Science, 324, 305 (1995).
TABLE I: Defect formation energy ($E_f$) for various doped BNNTs (We regard the BN sheet as a nanotube with radius $R = \infty$). For each of the three nanotubes, the first and second lines are the formation energies in the B rich or N rich environment respectively. Please refer to the text for the definition of $S_B^0$, $S^N_F$, and $A_B^0$. Energy is in eV.

|               | $E_f(S_B^0)+\mu_F$ | $E_f(S^N_F)+\mu_F$ | $E_f(A_B^0)+\mu_F$ |
|---------------|--------------------|--------------------|--------------------|
| BN(10,0)      |                    |                    |                    |
| B rich        | 5.887              | -3.891             | -3.846             |
| N rich        | 2.851              | -0.856             | -3.846             |
| BN(5,5)       |                    |                    |                    |
| B rich        | 5.851              | -3.907             | -3.995             |
| N rich        | 2.868              | -0.923             | -3.995             |
| BN sheet      |                    |                    |                    |
| B rich        | 7.196              | -2.453             | -3.188             |
| N rich        | 3.993              | 0.750              | -3.188             |
FIG. 1: (Color online) Three different configurations of F-doped BN(10,0) nanotubes: (a) one B substituted by one F atom ($S^B_F$), (b) one N substituted by one F atom ($S^N_F$), and (c) one F adsorbed on one B atom ($A^B_F$). Both top view and side view are shown.

FIG. 2: (Color online) Band structures for (a) pristine BN(10,0) nanotube, (b) BN(10,0) nanotube with one N substituted by one F atom, and (c) BN(10,0) nanotube with one F atom adsorbed on one B atom. The local DOS for the states induced by dopants are shown in the insets. The valence top or the Fermi level is taken as zero-energy point in (a) and (b) or (c) respectively.
FIG. 3: (Color online) Three different configurations BN(10,0) nanotubes doped with two F atoms: (a) two F atoms adsorb on two B sites, (b) two substitutional F atoms, and (c) one F atom adsorbed on one surrounding B atoms around the substituted N site. Both top view and side view are shown. Total DOS for these three structures are shown in (d), (e), and (f) respectively. The Fermi level (or valence top) is taken as zero-energy point in (d) and (f) (or (e)).