Electronic structure of nitrogen-doped carbon nanotubes under stress

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Abstract. Due to the demand for miniaturization and low energy consumption of electronic device, field-effect transistors based on carbon nanotubes have received extensive attention. However, the electronic properties of carbon nanotubes, especially when subjected to stress and doping, are not very clear. In this study, first-principles calculations are used to investigate the deformation of carbon nanotubes under the action of nitrogen doping and tensile stress, as well as the changes in electronic energy bands. The results show that nitrogen atom doping will reduce the tensile strength of carbon nanotubes and increase the conductivity of carbon nanotubes, while stress helps to open the band gap. Our research has guiding significance for the prediction of electronic properties of carbon nanotubes under doping and stress.

1. Introduction

The developments of the fifth-generation mobile communication technologies and artificial intelligence (AI) have induced eager demands of the next-generation electron devices with the requirements of miniaturization, low energy consumption and high frequency [1-2]. A conventional Si-based complementary metal-oxide-semiconductor (CMOS) transistor is found to have a theoretical limit of 5 nm owing to the rapidly reduction of carrier mobility with Si thickness [3-6]. Recently, some low-dimension materials, including carbon nanotube (CNT), graphene, transition metal disulfide (TMD) compounds and their heterstructure based field-effect transistors (FETs), have been proposed [7-10]. For instance, Desai et al. [4] designed double-layer MoS2 FET, and confirmed that a gate length of ~1 nm still can realize switch, meaning a good prospect to be a channel device. Hills et al. [10] prepared an all carbon nanotube transistors (more than 14,000) on an electronic chip, which can implement logical calculations.

Among various low-dimensional materials, the carbon nanotube should be one of the most valuable and promising materials due to the wide variety in the diameter and also chirality as well as the one-dimensional geometry. Owing to its dimensionality, some divergences in the DOS (density of states) remain to be solved. For example, the band gap of semiconductor CNT (N-M≠3k, where k is integer) is generally lower than 1 eV, which might be too low to use in FETs. What’s more, in the assembly of CNTs in a circuit wafer, some stresses could remain and the properties of CNTs would be changed.

In this study, we investigate the band structures and density of states of pure and nitrogen-doped carbon nanotubes of N=8 and N=9 (M=0), and the effects of stress on CNT are also calculated. Firstly, the structures of pure and nitrogen-doped carbon nanotubes are optimized using first principle calculations. Then, the band structures and charge transfer between nitrogen and carbon atoms are analyzed. We find doping with nitrogen makes the CNTs more likely to deform (be stretched) and reduces the band gaps. Meanwhile, the nitrogen atoms can enhance the DOS at Femi energy level, thus leading to a high conductivity.
2. Methods
All the calculations including geometry optimizations and electronic properties were performed in the CASTAP module of Material Studio 7.0, which is based on the first-principles pseudopotential plane-wave methods and the density functional theory (DFT). We set the cutoff energy to 10eV and the quality to medium for all calculation. More specifically, we choose the generalized gradient approximation (GGA) and the Perdew- Burke- Ernzerhof (PBE) function for the geometry optimization before adding any stress to the structure and choose the local density approximation (LDA) with CA-PZ function for the structure relaxations after adding stress and for all band structure calculations. In order to avoid unreasonable structural changes, we limit the stress under 1 GPa.

3. Results and discussions
The parameters for characterizing the structure of carbon nanotubes are (M, N), where M and N are integral times of the fundamental vector corresponding to the rotation axis. When N-M = 3k, where k is an integer, CNTs are metals, otherwise they are semiconductors. Here, we choose two kinds of carbon nanotubes: M = 0, N = 8 and 9. The former is an intrinsic semiconductor and the latter is a metal. Firstly, we study the structure of two kinds of carbon nanotubes under doping and stress, as shown in Fig. 1, where (a) - (h) is N = 8, (i) - (p) is N = 9, and the number of nitrogen atoms doped is 0,1,2 and 4 respectively. The stress applied on the CNTs is – 1 Gp, i.e. tensile stress.

After doping nitrogen atoms, the shape of carbon nanotubes changes significantly, but the shape of the pure carbon nanotubes is almost unchanged under the same stress, which indicates that nitrogen doping can reduce the tensile stiffness of carbon nanotubes.

![Figure 1. Structures of pure and nitrogen-doped carbon nanotubes, where (a) N=8, nitrogen 0 well relaxation, (b) N=8, nitrogen 0 under stress, (c) N=8, nitrogen 1 well relaxation, (d) N=8, nitrogen 1 under stress, (e) N=8, nitrogen 2 well relaxation, (f) N=8, nitrogen 2 under stress, (g) N=8, nitrogen 4 well relaxation, (h) N=8, nitrogen 4 under stress, (i) N=9, nitrogen 0 well relaxation, (j) N=9, nitrogen 0 under stress, (k) N=9, nitrogen 1 well relaxation, (l) N=9, nitrogen 1 under stress, (m) N=9, nitrogen 2 well relaxation, (n) N=9, nitrogen 2 under stress, (o) N=9, nitrogen 4 well relaxation, (p) N=9, nitrogen 4 under stress are displayed and the stress is -1 Gpa (stretch).]
In order to quantitatively analyze the deformation of carbon nanotubes under different N and doping conditions, lattice parameters of pure and nitrogen-doped carbon nanotubes under stress is shown in Table 1, where in well relaxed structure c is 4.26 Å. For example, when N = 8, the size of one doped nitrogen atom is 4.35, which increases to 4.42 at four doped nitrogen atoms. This is consistent with the results in Fig. 1, that is, nitrogen doping reduces the tensile strength of carbon nanotubes.

Table 1. Lattice parameters of pure and nitrogen-doped carbon nanotubes under stress, where in well relaxed structure c is 4.26 Å.

| Structure (stress of -1 Gpa) | c in one cell (Å) |
|-----------------------------|-------------------|
| N=8, nitrogen 0             | 4.32              |
| N=8, nitrogen 1             | 4.35              |
| N=8, nitrogen 2             | 4.38              |
| N=8, nitrogen 4             | 4.42              |
| N=9, nitrogen 0             | 4.33              |
| N=9, nitrogen 1             | 4.37              |
| N=9, nitrogen 2             | 4.38              |
| N=9, nitrogen 4             | 4.41              |

The properties of electronic band determine the performance of carbon nanotubes in electronic devices. Figures 2 and 3 show the band structures and density of states of pure and nitrogen-doped carbon nanotubes of N=8 and N=9, where the single figures are for (a) nitrogen 0 well relaxation, (b) nitrogen 0 under stress, (c) nitrogen 1 well relaxation, (d) nitrogen 1 under stress, (e) nitrogen 2 well relaxation, (f) nitrogen 2 under stress, (g) nitrogen 4 well relaxation, and (h) nitrogen 4 under stress. First of all, Fig. 2 (a) shows an obvious band gap, indicating that the N = 8 carbon nanotubes are intrinsic semiconductors. By comparing Fig. 2 (a) and (b), it can be found that the existence of stress has no significant effect on the electron energy band and density of states, especially the shape of the curve of density of States has little change. However, compared with Fig. 2 (a), (c), (e) and (g), it can be found that the introduction of nitrogen atoms makes the Fermi level move upward into the valence band, which significantly increases the density of states at the Fermi level.
Figure 2. Band structures and density of states of pure and nitrogen-doped carbon nanotubes of N=8, where the single figures are for (a) nitrogen 0 well relaxation, (b) nitrogen 0 under stress, (c) nitrogen 1 well relaxation, (d) nitrogen 1 under stress, (e) nitrogen 2 well relaxation, (f) nitrogen 2 under stress, (g) nitrogen 4 well relaxation, and (h) nitrogen 4 under stress.

Figure 3(a) shows the metallic N=9 carbon nanotubes, and we did not open the band gap when doping with nitrogen. In particular, after nitrogen doping, the density of states at the Fermi level increased slightly, indicating that the conductivity was enhanced. However, in the case of Fig. 3(b) without nitrogen doping but with stress, it seems that the band gap is opened.
Figure 3. Band structures and density of states of pure and nitrogen-doped carbon nanotubes of N=9, where the single figures are for (a) nitrogen 0 well relaxation, (b) nitrogen 0 under stress, (c) nitrogen 1 well relaxation, (d) nitrogen 1 under stress, (e) nitrogen 2 well relaxation, (f) nitrogen 2 under stress, (g) nitrogen 4 well relaxation, and (h) nitrogen 4 under stress.

In order to demonstrate the effects of nitrogen doping and applied stress, Table 2 shows the Band gaps and density of states at the Fermi level $D(\text{FE})$ in all cases. The band gap represents the metal or semiconductor properties of carbon nanotubes, and the density of states at the Fermi energy represents its electrical conductivity. We have seen that applying stress has certain benefits to the opening of the band gap. For example, the band gap of N=8, nitrogen 0, is 0.173 eV, which increases to 0.449 eV after applying stress. N=9, the original band gap of nitrogen 0 is 0, and a band gap of 0.342 eV appears after stress is applied.

At the same time, the introduction of nitrogen atoms will enhance the conductivity of carbon nanotubes, but with the increase of the concentration of nitrogen atoms, the change trend of the conductivity is non-monotonic. E.g. When N=8, the incorporation of a nitrogen atom increases the density of states at the Fermi energy from 0.4 to 6.39 1/eV, but continuing to increase the concentration of nitrogen atoms causes the density of states to drop to 3.6 and 5.6 1/eV. A similar situation was found for carbon nanotubes with N=9.
Table 2. Band gaps and density of states at the Fermi level $D(E_F)$.

| Structure                      | Band gaps (eV) | $D(E_F)$ (1/eV) |
|-------------------------------|---------------|-----------------|
| N=8, nitrogen 0, relaxation   | 0.173         | 0.4             |
| N=8, nitrogen 0, stress       | 0.449         | 1.15            |
| N=8, nitrogen 1, relaxation   | 0             | 6.39            |
| N=8, nitrogen 1, stress       | 0             | 8.99            |
| N=8, nitrogen 2, relaxation   | 0             | 3.60            |
| N=8, nitrogen 2, stress       | 0             | 2.49            |
| N=8, nitrogen 4, relaxation   | 0             | 5.60            |
| N=8, nitrogen 4, stress       | 0             | 4.78            |
| N=9, nitrogen 0, relaxation   | 0.342         | 2.46            |
| N=9, nitrogen 0, stress       | 0             | 6.63            |
| N=9, nitrogen 1, relaxation   | 0             | 5.87            |
| N=9, nitrogen 1, stress       | 0             | 7.78            |
| N=9, nitrogen 2, relaxation   | 0             | 5.87            |
| N=9, nitrogen 2, stress       | 0             | 7.08            |
| N=9, nitrogen 4, relaxation   | 0             | 6.08            |

In order to understand the influence of doping and stress on the electronic energy band of carbon nanotubes, we calculated the electronic differential density under several conditions. Figure 4 shows the charge transfer between nitrogen and carbon atoms after doping, where (a) and (e) are 1 nitrogen well relaxation, and (b) and (f), (c) and (g), (d) and (h) are 1 nitrogen under stress, 2 nitrogen under stress, 3 nitrogen under stress for N=8 and 9. The blue isosurface represents charge accumulation, and the yellow isosurface represents charge consumption. It can be seen that the covalent bond between nitrogen atoms is the electron gathering area, and the middle area of the six-membered carbon ring is the electron consuming area. The blue isosurface of the carbon atom that forms a bond with the nitrogen atom is significantly closer to the nitrogen atom, indicating that the nitrogen atom has taken away the charge of the carbon atom, which is also the reason why the doping of the nitrogen atom affects the electron energy band.
4. Conclusions
In the present study, we used the first-principles method to calculate the electronic band structure of different zigzag carbon nanotubes (N=8 and N=9) under nitrogen doping and stress. The results show that nitrogen atom doping will significantly reduce the tensile strength of carbon nanotubes. Stress has the effect of opening and increasing the band gap. Nitrogen atom doping will increase the conductivity of carbon nanotubes, but a high doping concentration may not have a stronger effect on the conductivity. Nitrogen atoms have the ability to take away the charge of carbon atoms, which is the reason that affects the electron energy band.

References
[1] Deblina Sarkar, Wei Liu, Xuejun Xie, et al. MoS2 Field-Effect Transistor for Next-Generation Label-Free Biosensors. ACS Nano, 2014, 8(4):3992.
[2] Godfrey Akpakwu, Bruno Silva, Gerhard P. Hancke, et al. A Survey on 5G Networks for the Internet of Things: Communication Technologies and Challenges. IEEE Access, 2017, 5(12):3619-3647.
[3] Kawaura H, Sakamoto T, Baba T. Observation of source-to-drain direct tunneling current in 8 nm gate electrically variable shallow junction metal–oxide–semiconductor field-effect transistors. Applied Physics Letters, 2000, 76(25):3810.
[4] Desai S B, Madhavapathy S R, Sachid A B, et al. MoS2 transistors with 1-nanometer gate lengths. Science, 2016, 354(6308):99-102.
[5] Liu L, Lu Y, Guo J. On Monolayer, Field-Effect Transistors at the Scaling Limit. IEEE Transactions on Electron Devices, 2013, 60(12):4133-4139.
[6] Yoon Y, Ganapathi K, Salahuddin S. How good can monolayer MoS2, transistors be?. Nano Letters, 2011, 11(9):3768-3773.
[7] Feng Zhang. On the Tunability of Short-Channel Effects in MoS2 Field-Effect Devices. Nano Letters, 2014, 15(1):301.
[8] Bilu Liu, Yuqiang Ma, Anyi Zhang, et al. High Performance WSe2 Field-Effect Transistors via Controlled Formation of In-Plane Heterojunctions. Acs Nano, 2016, 10(5):5153.
[9] Fathipour S, Hwang W S, Kosel T, et al. Exfoliated MoTe2 field-effect transistor. Device Research Conference. IEEE, 2013.
[10] Hills G, Lau C, Wright A, et al. Modern microprocessor built from complementary carbon nanotube transistors. Nature, 2019, 572(7771):595-602.