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Citation: *Appl. Phys. Lett.* **102**, 153107 (2013); doi: 10.1063/1.4802884

View online: <http://dx.doi.org/10.1063/1.4802884>

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## Experimental identification of p-type conduction in fluoridized boron nitride nanotube

Jing Zhao,<sup>1,2,a)</sup> Wuxia Li,<sup>1,b)</sup> Chengchun Tang,<sup>2</sup> Lin Li,<sup>1</sup> Jing Lin,<sup>2</sup> and Changzhi Gu<sup>1,b)</sup>

<sup>1</sup>Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

<sup>2</sup>School of Materials Science and Engineering, Hebei University of Technology, Tianjin 300130, China

(Received 5 March 2013; accepted 8 April 2013; published online 19 April 2013)

The transport properties of F-doped boron nitride nanotube (BNNT) top-gate field effect devices were investigated to demonstrate the realization of p-type BNNTs by F-doping. The drain current was found to increase substantially with the applied negative gate voltage, suggesting these devices persist significant field effect with holes predominated; it also suggests that F-doping remarkably modified the band gap with F atoms preferred to be absorbed on B sites. Parameters, including the resistivity, charge concentration, and mobility, were further retrieved from the I-V curves. Our results indicate that device characterization is an effective method to reveal the specific properties of BNNTs. © 2013 AIP Publishing LLC [<http://dx.doi.org/10.1063/1.4802884>]

One-dimensional semiconductor nanostructures are receiving increasing attention due to their flagship qualities that are crucial for nanoapplications.<sup>1</sup> As a wide bandgap semiconductor, boron nitride nanotubes (BNNTs) have continuously attracted ever-wider attention<sup>2,3</sup> since they are light in weight, stable at high temperatures, resistant to oxidation.<sup>4,5</sup> Most interestingly, though BNNTs are structurally similar to carbon nanotubes (CNTs), they are different from CNTs in many aspects.<sup>6,7</sup> In particular, BNNT is an electrical insulator with a bandgap of ca. 5.5 eV, basically independent of tube chirality, size, and morphology.<sup>8</sup> This implies perfect uniformity of electrical behavior is achievable in such materials, which is unavailable in CNTs.<sup>9,10</sup> The unique electrical properties, the high thermal stability, and the outstanding chemical inertness of BNNTs provide them with amazing prospects of fabricating nanodevices competent to operate in harsh environments, as well as to serve as one of the most promising building blocks in the construction of ultraviolet-blue light-emitting diodes, lasers, detectors, high temperature and high power devices, and even spintronics.<sup>11,12</sup> However, pristine BN structures are unsuitable for many functional applications due to their large insulating band gap. To circumvent this hurdle, the most popular strategy is to modify its electronic structure.

Quite a few theoretical and experimental investigations have been performed in the past few years to synthesize,<sup>3,13</sup> predict, and modify the electronic structures of BNNTs.<sup>8,14,15</sup> Doping and surface chemisorptions are recognized as the effective methods to tune the electronic structure of BNNTs. Previous experimental studies on functionalization of BNNTs have mainly focused on the B-N-C system through the sophisticated control of C content.<sup>16–20</sup> Based on the fact that fluorine (F) is highly electronegative element and has excessive valence electrons compared to B and N, BN doped with F was supposed to be n-type semiconductors.<sup>15</sup> And for

nano-electronic device applications, fluorination has been one of the most effective pathways to tune the transport properties of BNNTs. However, the behavior of dopants in semiconductors is often far from trivial. Xiang *et al.*<sup>21</sup> reported that the F-doped BNNTs with large conductivity might be of p-type due to the adsorbed F atoms. Recently, Tang *et al.*<sup>15</sup> have reported the substantial reduction of the resistivity of F-doped BNNTs, which was found to be three orders of magnitude smaller than that of the undoped BNNTs. Thus, questions as could the F-doping really result in the formation of p-type BNNTs, and how to judge whether the F-doped BNNTs are p-type semiconductors, must be addressed for fundamental physics study as well as for practical applications. To facilitate the development of devices based on functionalization, it is imperative to explore a facile route capable of efficiently prediction of the properties of the modified BNNTs.

We note that undesirable chemisorption on F-doped BNNT surfaces, even absorption of the ambient gases, primarily oxygen,<sup>22</sup> may have significant influence on the electronic transport of F-doped BNNT field-effect transistors (FETs) when they are back-gated. In addition, top-gate FETs are more desirable for integrated circuit fabrication.<sup>23</sup> Therefore, in this letter, top-gate F-doped BNNT field effect devices were fabricated on SiO<sub>2</sub>/Si substrates with Al<sub>2</sub>O<sub>3</sub> dielectric layer as the gate barrier. The tubes used here were prepared followed the method we previously reported.<sup>15</sup> The drain current was found to increase substantially when the gate voltage was changed from 0 V to −15 V, which indicated that these devices persisted significantly applied gate voltage dependence with holes dominated. Other parameters, such as the resistivity, the charge concentration, and the mobility of the tubes were retrieved from the I-V curves; the variation trends of these parameters with respect to the applied gate voltage were investigated. Our results experimentally confirm that the adsorption of F atoms on B sites is more stable than that on N sites; meanwhile, field effect I-V characterization is an effective method to identify the doping types of nano-materials.

<sup>a)</sup>E-mail: zhaojing@aphy.iphy.ac.cn

<sup>b)</sup>Authors to whom correspondence should be addressed. Electronic addresses: liwuxia@aphy.iphy.ac.cn and czgu@aphy.iphy.ac.cn

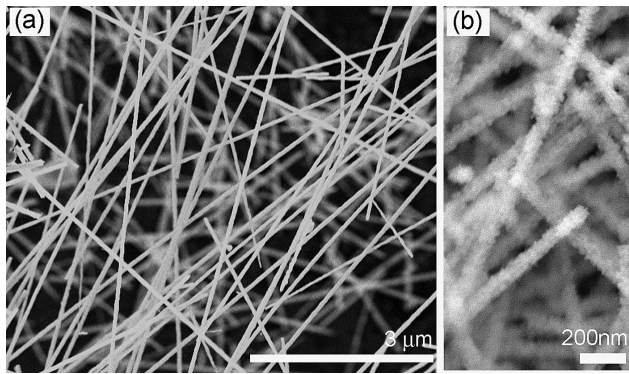


FIG. 1. A typical scanning electron microscope image of F-doped BNNTs (a) and that at higher magnification showing details of the tube wall (b).

Figure 1(a) shows the typical scanning electron microscope (SEM) image of the F-doped BNNTs, which having a diameter in the range of 70–100 nm and the length is in the order of a few microns. These tubes were synthesized by simultaneously introducing F atom during the tubes growth. The general synthesis method and growth mechanism have been elaborated elsewhere.<sup>15</sup> Figures 2(a) and 2(b) show the sketch and the top-view SEM image of a fabricated device, respectively. The device was constructed by electron beam lithography related techniques. First, the as-grown F-doped BNNTs were dispersed in alcohol and then spin-coated on the substrate. After locating a single F-doped BNNT by SEM, the source and drain electrodes with Ni/Au layers (5 nm/90 nm) were formed on both ends of a single F-doped BNNT by electron beam lithography and thermal evaporation, followed by a lift-off process. After that, a 30 nm dielectric layer was deposited conformably on the substrate as well as on the F-doped BNNT channel by atomic layer deposition (ALD). It is noted that the F-doped BNNT channel was surrounded by the thin film, avoiding damages may be caused in further procedures for device fabrication. During the ALD process, the same temperature (250 °C) and pressure (260 mTorr) were kept for high-quality Al<sub>2</sub>O<sub>3</sub> gate dielectric layer deposition. Finally, a gate electrode was formed on the top of the 30 nm Al<sub>2</sub>O<sub>3</sub> gate oxide layer at the central part of the F-doped BNNT channel, then with repeating the EBL, metal deposition and lift-off processes, a top-gate BNNT field effect device was obtained as shown in Fig. 2(b). The single F-doped BNNT is 10 μm in length, 80 nm in diameter and the source-drain electrode is 1 μm in width at both ends of the nanotube, and the top-gate electrode is 0.9 μm in width. The I-V characteristics of the fabricated devices were measured using a probe stage equipped with

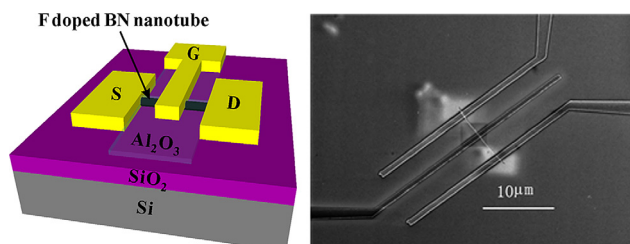


FIG. 2. (a) The schematic diagram of the top-gate field effect device and (b) the top-view scanning electron microscope image of a fabricated F-doped BNNT device.

semiconductor characterization system (Keithley 4200) in an ambient environment. By successive measurements of a particular device with repeating the process of probe-pressing, I-V curve recording, and probe-withdrawing, reliable I-V data can be achieved. We would like to point out that although the Al<sub>2</sub>O<sub>3</sub> dielectric layer was also deposited on the source and drain electrodes, it is easy to be punctured through with the measuring probes. Alternatively, for electrical connection, techniques of photolithography or electron beam lithography, followed by Al<sub>2</sub>O<sub>3</sub> dry etching, were used to open windows through the Al<sub>2</sub>O<sub>3</sub> layer to provide direct contact of the probe with the metal source and drain pads, which technically, is a more accurate and reliable approach compared with the probe puncturing method.

Fig. 3 presents a series of successively recorded  $I_{ds}$ - $V_{ds}$  curves along with an increase in applied  $V_{gs}$  performed on a fabricated typical top gate F-BNNT field effect device. The drain current increased with increasing the drain voltage at room temperature and it was symmetric when no  $V_{gs}$  was applied; then when  $V_{gs}$  was increased from 0 V to -15 V, at a particular positive  $V_{ds}$ , there was remarkable increment of  $I_{ds}$  at a medium bias regime, and the  $I_{ds}$ - $V_{ds}$  curves became asymmetric. The data clearly reveal that hole current dominates the electric transport of the F-doped BNNT, since negative  $V_{gs}$  increases  $I_{ds}$  and the Fermi level in the metal is asymmetrically lined up with the bands of the F-doped BNNT, resulting in a smaller barrier between the metal Fermi level and the valence band of the F-doped BNNT. The electronic properties of fluorinated BNNTs by first-principles calculations revealed that F atoms prefer to substitute N atoms, resulting in substantial changes of BN layers.<sup>21</sup> Also, since F substitutional doping only results in deep impurity states, it does not affect the conductivity of the doped materials. On the other hands, BNNTs with adsorbed F atoms are *p*-type semiconductors with much enhanced conductivity.<sup>21</sup> Our experimental results clearly demonstrate that F-doped BNNTs have substantially enhanced conductivity over the pristine counterparts, they are thus *p*-type semiconductors, consistency with the theoretic prediction.

For a better understanding of the properties of the F-doped BNNTs, before retrieving the parameters, e.g., the resistivity, the hole concentration, and the hole mobility of

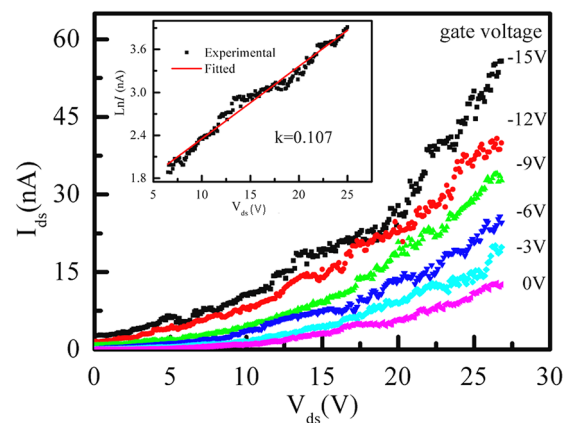


FIG. 3.  $I_{ds}$ - $V_{ds}$  characteristics obtained with  $V_{gs}$  changed from 0 to -15 V with a step size of -3 V. The inset is the natural logarithmic  $I_{ds}$  as a function of the applied forward bias voltage.



the F-doped BNNTs, electron energy lose spectroscopy (EELS) installed in a high resolution transmission microscope system was used to reveal the F concentration. An atomic ratio less than 5% was obtained from the EELS spectra. A few percent of deviation of this value might persist since the amount of F is relatively low. In semiconductor realm, doping concentration is a crucial parameter of a functional material, towards the construction of devices and circuits with high performance; but different from bulk materials, the accurate control of doping in nanomaterial system is still a challenge, and the characterization of the doping concentration is also much more trivial. Followed the method presented by Zhang *et al.*,<sup>24</sup> in our experiment, the two terminal Au/Ni-F-BNNT-Ni/Au nanosystem was considered as the serial integration of two back to back Schottky diodes with a pure resistor in between. Thus, when a very low voltage was applied, the two diodes were both “off,” the current passing through the system was very small and the total voltage was distributed mainly on the two Schottky barriers. At higher bias voltage with  $V$  reached at about 2 V, the voltage dropped across the reverse-biased Schottky barrier increased rapidly and became dominating. Until at about 8 V, the current began to become notable and the voltage on the nanowire became non-negligible, while the voltage dropped across the forward biased Schottky barrier remained small. When further increasing the bias, the thickness reduction of Schottky barrier for hole tunneling became less effective and the voltage dropped across this barrier started to saturate at  $V$  of about 12 V. The voltage on the nanotube increased almost linearly with the bias and became the dominating term when  $V$  was around 22 V. In this large bias regime, the I-V curve can be differentiated to obtain the resistance of the nanotube, as can be given by the equation below:

$$R = \frac{dV_N}{dI} \approx \frac{dV}{dI}. \quad (1)$$

Furthermore, the semiconductor parameters can be retrieved from the I-V curves in the intermediate bias regime where the reverse-biased Schottky barrier dominates the total current  $I$ , which can be written as<sup>24</sup>

$$\ln I = \ln(SJ) = \ln S + V \left( \frac{q}{kT} - \frac{1}{E_0} \right) + \ln J_S, \quad (2)$$

where  $J$  is the current density through a Schottky barrier,  $J_S$  is a slowly varying function of an applied bias, and  $S$  is the contact area associated with a barrier; in turn,  $E_0$  is given by the equation:  $E_0 = E_{00} * \coth(E_{00}/kT)$ , where  $E_{00} = \hbar q/2 (n/m^* \epsilon)^{1/2}$ ,  $n$  is the hole concentration,  $m^*$  is the effective hole mass of the F-doped BNNT, and  $\epsilon$  is the dielectric constant. The logarithmic plot of the current  $I$  as a function of the bias  $V$  gives an approximately straight line with a slope of  $q/(kT) - 1/E_0$ , as shown in the inset in Fig. 3. Thus, the hole concentration  $n$  can be acquired via  $E_0$ ; further, the carrier mobility  $\mu$  can be obtained. The applied gate voltage correlated resistance, resistivity, hole concentration, and carrier mobility of the F-doped BNNT were extracted and summarized in Table I.

TABLE I. Applied gate voltage dependent parameters for F-doped BNNTs.

Gate voltage	0 V	-3 V	-6 V	-9 V	-12 V	-15 V
Resistance (GΩ)	3.19	1.48	1.18	0.86	0.76	0.57
Resistivity (Ωcm)	85.0	39.44	31.58	22.95	20.14	15.09
Hole concentration ( $\times 10^{16} \text{ cm}^{-3}$ )	3.01	2.91	2.33	2.42	2.30	2.37
Mobility ( $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ )	2.45	5.45	8.49	11.27	13.48	18.82

It can be seen from Table I that with increasing the applied gate voltage, the resistance and the hole concentration of the F-doped BNNTs decreased while the mobility increased. This is because the higher the applied gate voltage, the more the induced conducting charges, and the higher the field in the conducting channel, which make the nanotube less resistive, as expected. It is well-known that pristine BNNT is electrically insulating. Bai *et al.* reported an *in-situ* elastic deformation induced electronic structure modification of undoped BNNTs, which can be tuned from insulating to semiconducting through a bending deformation. Differently, they found that with increasing the bending curvature of the suspended BNNT, the resistivity and hole concentration of the nanotube increased while the mobility decreased, which is possibly due to the bending induced in-shell defect formation (e.g., voids, vacancies, antisite atoms, etc.).<sup>25</sup> In their case, since defects creation and strain are the main factors that led to the change of the electronic structures of pure BNNT, increasing the number of defects in the system could very likely increase the charge scattering probability when the chargers transport through the bent BNNT, thus intense bending can result in increased resistivity but reduced mobility. As they expected, the defects were observed to appear on bending and disappear after a load release. In device applications, usually a high charger concentration and mobility are required for high device performance. Thus, the observed field effect on the F-doped p-type top-gate device presented here is favorable for a future application.

We fabricated top-gate F-doped BNNT field effect devices by electron beam lithography (photolithography) process, and characterized their field effect characteristics. The I-V properties showed significant applied gate voltage dependence: the drain current  $I_{ds}$  increased as the gate voltage,  $V_{gs}$ , varied from 0 V to -15 V, indicating that holes are the dominated carriers in the transportation. It also confirms that F-doping introduced during growth resulted in p-type BNNT semiconductors, thus field effect can be observed in a three terminal gated configuration. However, for metallic and other types of materials, it may not necessary to follow such an approach. Hole concentration of  $3.01 \times 10^{16}$  was achieved and it can be effectively modulated by the applied gate voltage. These results suggest that device fabrication and analyzing is an effect approach for electrical and semiconducting properties characterization of BNNTs.

The authors would like to thank Zhaosheng Hu for very valuable discussions. This work was supported by the Outstanding Technical Talent Program of the Chinese Academy of Sciences, the National Natural Science Foundation of China under Grants Nos. 91123004, 11104334,

50825206, 10834012, 60801043, 10974041, and 51172060; and the National Basic Research Program (973) of China under Grant Nos. 2009CB930502 and 2011CB612301.

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