Journal of the Korean Physical Society, Vol. 42, February 2003, pp. S137∼S142

Band Gap Modulation of a Carbon Nanotube by Hydrogen Functionalization

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We have investigated a modification of electronic structures of a carbon nanotube by hydrogen functionalization. Carbon nanotubes were exposed to atomic hydrogen which was generated by a hot tungsten filament in the vacuum chamber. Current-voltage characteristics clearly showed a band gap widening after hydrogenation. This was explained by an enhancement of sp^3 hybridization with hydrogen chemisorption on the tube wall. Our density functional calculations also predicted a strong chemisorption with pi electron modulation and the band gap widening upon hydrogenation.

PACS numbers: 71.15.Mb,72.80.Rj,73.50.-h
Keywords: Nanotube, Functionalization, Transistor

I. INTRODUCTION

The electronic structure of carbon nanotubes (CNTs) is determined exclusively by the chirality (n,m) [1]. Achiral (n,n) is called an armchair nanotube, revealing metallic properties, and (n,0) is called a zigzag nanotube. When n is a multiple of three, they become zero-gap semiconductors and otherwise they become semiconducting nanotubes with a finite size of the band gap. The band gap decreases with increasing diameter of the tube, approaching zero at infinite diameter, *i.e.*, graphite. Chiral (n,m), where, n≠m, n-m=3k with an integer k, they become metallic tubes, and otherwise they become semiconducting nanotubes. To our knowledge, there is no way to control the chirality selectively by the conventional synthesis approaches [2–4]. This has often been a bottleneck in the application of CNTs to electronic devices such as nanotransistors and memories which require preexisting semiconducting CNTs [5]. It is therefore necessary to produce CNTs with a large band gap if possible, a prerequisite for such devices to be operable at room temperature.

The current fabrication of the nanotube transistor relies on the lithography. For instance, carbon nanotubes dispersed in the solvent can be sprayed on very thin oxide layer formed on Si substrate. Once the solvent was evaporated, metal electrodes can be deposited by lithography approach to form source-back gate (oxide)-drain, where the current flows through the nanotube. Since metallic and semiconducting nanotubes are mixed in the solution, there is always a chance to find metallic nanotubes which do not reveal a gating effect and therefore cannot be used as transistors. This is a serious drawback for real application to for instance, memory devices. While CNT heterojunctions formed with different chiralities [6] and cross junction [7] have been introduced, which demonstrated the required performance for CNT nanotransistors, these rely on an accidental junction formation during sample preparation. One alternative approach is to transform the electronic structure of the CNT to one with a large band-gap semiconductor by a post-process treatment.

Functionalization of a CNT wall sometimes leads to serious modification of the electronic structure. For instance, fluorination of the CNT modifies the electronic structures to be either metallic or semiconducting, depending on the coverage and method of fluorine decoration [8–11]. This approach induces a large strain on the tube wall and sometimes deteriorates the CNT wall. A more reliable way to transform from metallic to semiconducting CNTs with a minimal alteration on the CNT wall stability is highly desirable.

Here we present a method for CNT functionalization by exposing CNTs to hydrogen atoms. To demonstrate the effect of hydrogen functionalization, we fabricate a CNT-metal junction on silicon substrate by electron-beam lithography, where one half of the CNT was buried in SiO_2 and the other half is exposed to air. The exposed CNT was functionalized by the atomic hydrogen and the

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half of the CNT buried in SiO_2 remained intact. This clearly showed a rectifying effect which was interpreted in terms of a robust formation of intramolecular junction in the middle of the tube by hydrogenation.

II. EXPERIMENTAL AND THEORETICAL APPROACHES

The CNT powder generated by chemical vapor deposition was dispersed in a chloroform solution. The droplet containing CNTs was placed on a marked silicon substrate with thermally grown oxide layer of 500 nm thickness. After drying, the metal electrodes (Au-Ti) were patterned on appropriately selected CNT by electron-beam lithography. A very thin layer of Ti was intentionally deposited on the nanotube to reduce the contact resistance. The diameter of the CNT was about 2 nm as determined from atomic-force-microscopy measurement. The contact resistance was lowered by rapid thermal annealing at 800 °C for 30 seconds in vacuum [12,13]. Half of the chosen CNT was then covered by SiO_2 layer of 100 nm. The typical I-V characteristics were measured at various temperatures in vacuum. Prior to hydrogenation of the CNT, the degassing was done for 6 hours at 300 °C. Atomic hydrogen was supplied by flowing hydrogen gas through a hot tungsten filament that was located 2 cm away from the sample. This increased the sample temperature to 100 °C during hydrogenation. Hydrogenation was maintained at 10^{-5} torr for a few hours. We ensured from atomic force microscopy that the metal electrodes remained intact after hydrogenation. Once the hydrogenation was complete, the chamber was evacuated again to 10^{-8} torr. The I-V characteristics were then measured again.

In order to understand the nature of hydrogen chemisorption, we performed density functional calculations within the local density approaximation (LDA) and generalized gradient approximation (GGA) The exchange-correlation energy in the LDA was parameterized by Perdew and Zunger's scheme [14] and Perdew and Wang's exchange functional [15] was adopted in GGA calculations. The ultrasoft pseudopotential for carbon atom was generated using Vanderbilt scheme [16]. and the routine pseudopotential for hydrogen atom was generated using Troullier and Martins's scheme [17]. The electronic wavefunction was expanded in a planewave basis. The kinetic energy cutoff was chosen to be 26 Ry. Four k-point sampling was done in the irreducible Brillouin zone along the tube axis. Convergence test was done with larger cutoff and more k-point sampling in GGA. The change in overall band shape was negligible but the band gap was increased by 0.02 eV with a larger kinetic energy cutoff (32 Ry).

We chose(9,0) zigzag nanotubes to calculate the band structures and density of states. The tube-tube separation distance was 5 Å, larger than van der Waals interactions of 3.4 Å, to neglect the tube-tube interactions.

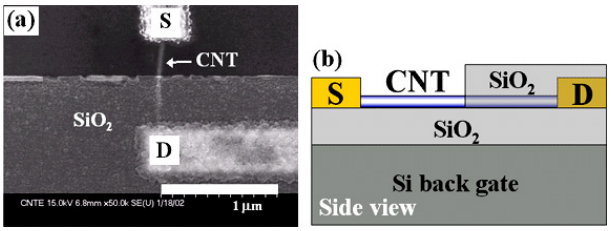

Fig. 1. (a)SEM image and (b)schematic diagram of the CNT-field effect transistor(FET). This clearly shows that a half of the nantoube was buried in SiO_2 overlayer of 100 nm.

III. RESULTS AND DISCUSSION

Figure 1 shows the scanning electron microscope (SEM) image of our nanotube connected by two metal electrodes and the corresponding schematic diagram. This clearly shows that a half of the nantoube was buried in SiO_2 overlayer of 100 nm. Once this was fabricated, a direct measurement of I-V characteristics between source and drain gave a large contact resistance of usually a few tenth MΩ. This was significantly reduced to a few tenth KΩ after thermal annealing at 600 ∼ 800 °C for 30 sec, which was attributed to the formation of TiC layers between metal and nanotube. [12,13].

Figure 2 shows the source-drain currents as a function of voltage measured at room temperature. The pristine sample before hydrogenation shows a straight line, *i.e.*, an ohmic behaviour with a resistance of 10 MΩ near zero source-drain voltage. In contrast with this, the hydrogenated CNT shows a negligible current at negative bias and an abrupt current increase with increasing positive

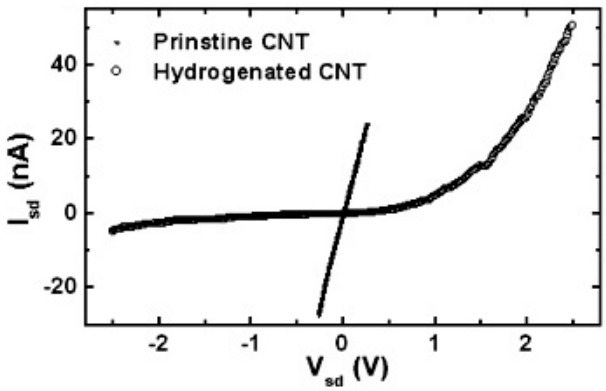

Fig. 2. IV characteristics at room temperature. The pristine sample before hydrogenation shows a straight line, *i.e.*, an ohmic behaviour.In contrast with this, the hydrogenated CNT shows a negligible current at negative bias and an abrupt current increase with increasing positive bias, revealing a rectifying effect.

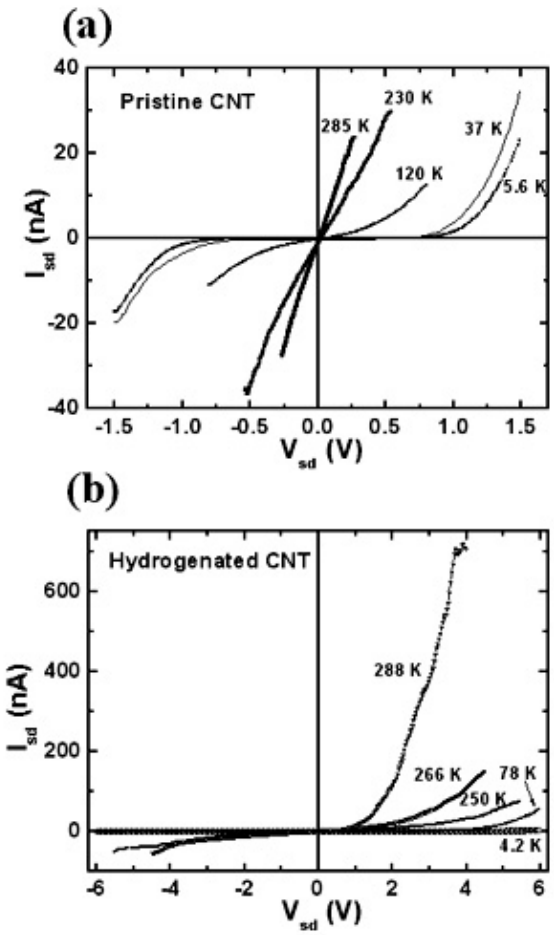

Fig. 3. The temperature-dependent I-V characteristics of the (a) pristine and (b) hydrogenated samples.The current is suppressed with lowering temperatures, increasing the turn-on voltage in the pristine sample.The rectifying behaviour for hydrogenated samples is clearly seen at all temperature ranges, as shown in figure (b).

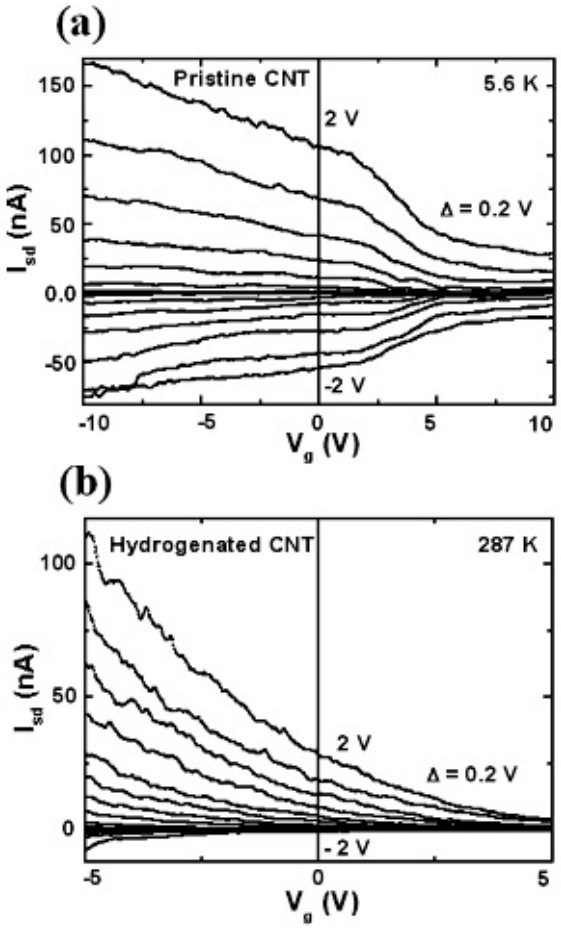

Fig. 4. Gating effect. The drain current as a function of a gate voltage for given drain voltages (a) at 5.6 K for pristine CNT and (b) at 287 K for hydrogenated CNT.The increment of drain voltage is 0.2 V. The hydrogenated sample shows the rectifying effect more prominently, as can be seen in Figure (b), where the negligible currents flow at negative drain voltages.

bias, revealing a rectifying effect. The anisotropy, which can be defined as

$$a = \mid (V_d = 2V)/I(V_d = -2V) \mid, \quad (1)$$

is 10. This value remains almost the same over the whole range of drain voltage.

Figure 3 shows the temperature-dependent I-V characteristics of the pristine and hydrogenated samples. The current is suppressed with lowering temperatures, increasing the turn-on voltage in the pristine sample. This indicates that (i) the nanotube is semiconducting with a finite band gap and (ii) the contact-barrier height between the metal and nanotube is comparable to room temperature. The asymmetric current flow shown particularly at low temperature may be attributed to the existence of an asymmetric contact barrier in two metal-CNT contacts. The current flow is severely suppressed, increasing the turn-on voltage in the hydrogenated sample. Note that the scale in the drain voltage is expanded to 6 V in the hydrogenated sample. The rectifying behaviour is clearly seen at all temperature ranges, as shown in figure 3(b). The differential conductance shows that the energy gaps of the pristine and hydrogenated samples are 0.8 and 4.4 eV, respectively [19].

Since the nanotube is semiconducting, the gating effect should be seen.

Figure 4 shows the drain current as a function of a gate voltage for given drain voltages at 5.6 K. More currents flow at positive drain voltages in the pristine sample, again reflecting the existence of asymmetric contact barriers. The current flow even at zero gate voltage may be attributed to the leakage current from the gate. The quality of the oxide layers can be improved to remove such an effect. The current is suppressed at positive gate voltage, indicating that it is the hole carrier which governs the transport of the nanotube. This confirms the previous reports that the presence of oxygen gases either

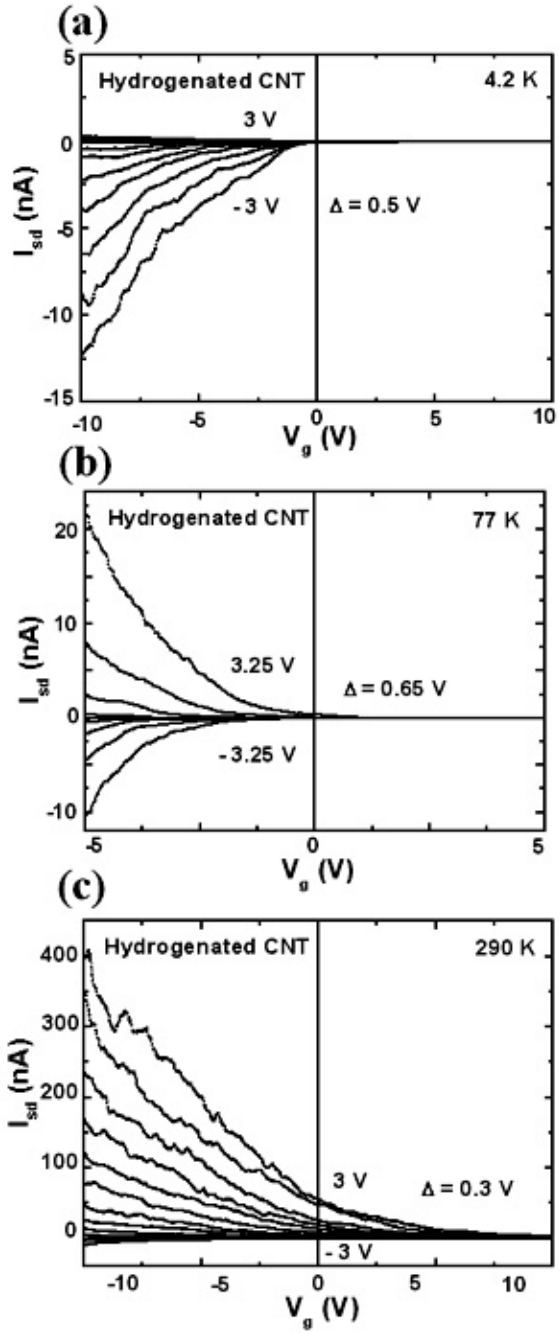

Fig. 5. The temperature dependence of the gating effect measured at (a) 4.2 K, (b) 77 K, and (c) 290 K. At low temperature, the small reverse current of a few tenth nA flows at negative gate voltage.

on the tube wall or at the metal-CNT contact depletes the charge in the tube, leaving holes in the tube [18]. The hydrogenated sample shows the rectifying effect more prominently, as can be seen in figure 4(b), where the negligible currents flow at negative drain voltages. We emphasize that the rectifying effect is shown more clearly even at 287 K in the hydrogenated sample.

It is interesting to see that the I-V characteristics still

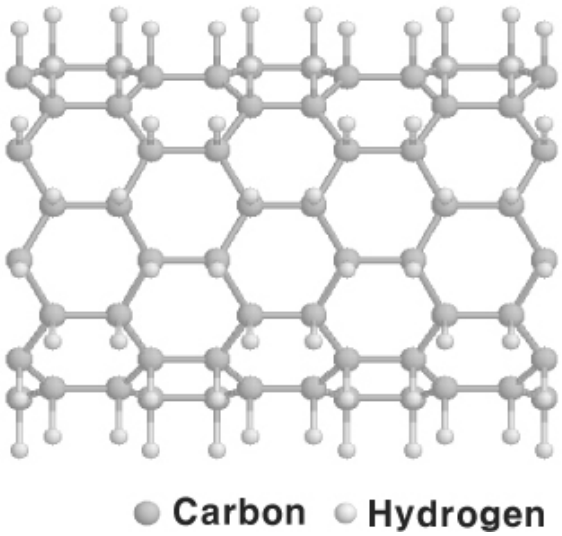

Fig. 6. Hydrogenated CNT in ball and stick model. Large dark-grey ball is carbon and small light-grey is hydrogen.

show the hole-carrier even in the hydrogenated sample. This is an evidence of the presence of oxygen gases that oxygen gases are persistently present in our sample, even though we took the degassing process for a few hours or they may be redeposited after hydrogenation.

The temperature dependence of the gating effect is shown in Figure 5. At low temperature, the small reverse current of a few tenth nA flows at negative gate voltage, whereas the forward current is severely suppressed, as shown in Figure 5(a). The reverse current is persistent even at room temperature. However, a large forward current flows at high temperature. The origin of such an inversion of the current flow is not clear at this moment. It may be conjectured that an asymmetric gate is formed near the source and drain electrodes so as to invoke the inversion current.

One may imagine that an intramolecular junction is formed upon hydrogenation. Originally small-gap semiconducting nanotube becomes large-gap semiconducting one with hydrogenation such that two semiconductors form intramolecular junctions. In order to understand the band-gap opening by hydrogenation, we now calculate the band structures and density of states. It has been suggested that atomic hydrogen can be chemisorbed on the nanotube wall [21–23].

Figure 6 shows hydrogenated zigzag (9,0)nanotubes in ball and stick model. We assume that all top carbon sites are saturated by hydrogen atoms. Atomic hydrogen chemisorbs with relatively strong binding energy of -2.65 eV/C-H, half of a methane molecule [22]. The diameter of the hydrogenated nanotube is also expanded by 13 %, compared to the pristine nanotube.

The zigzag (9,0)nanotube has a zero energy gap, *i.e.*, unoccupied and occupied states overlap at the Fermi level, as shown in Fig. 7. The density of states, how-

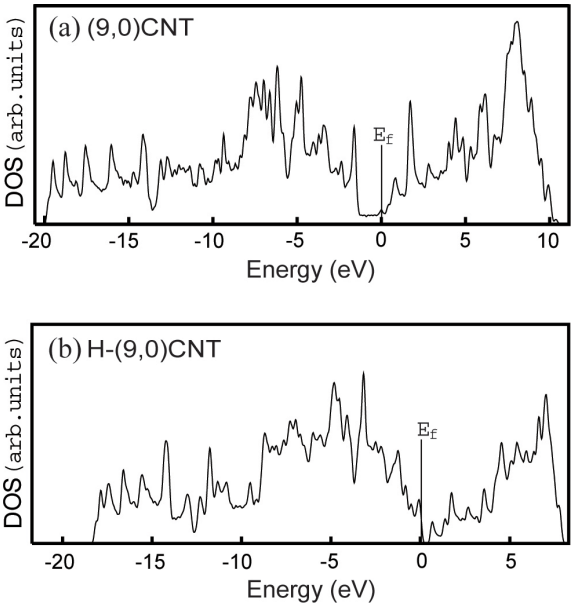

Fig. 7. The density of states in zigzag (9,0) (a) pure and (b) hydrogenated nanotubes.

ever, shows a small bump which was a fake due to the overlapping of two states. A clear band gap is observed in the hydrogenated nanotube.

Since we used small kinetic energy cutoff with ultrasoft pseudopotential in the LDA calculations, the energy gap is underestimated. However, this calculation reveals at least the general trend of the band gap upon hydrogenation. Strong chemisorption enhances the sp^3 hybridization in the carbon atoms, inducing more corrugations in the π electrons. The enhancement of the π states up to -9 eV can be also seen in the density of states. The valence band width is narrowed in the hydrogenated nanotube.

We note that the width of the first subbands between unoccupied and occupied bands is also narrowed. We can imagine that the band-gap opening in the half of the nanotube induces an intramolecular junction, giving a rectifying effect. One may estimate the contact barrier height and junction barrier height using Arrhenius plot and thermionic electron emission model [19].

IV. CONCLUSION

We have investigated modification of electronic structures by hydrogen functionalization. We observed a clear rectifying effect in the hydrogenated CNT, where half of the CNT was buried in SiO_2 overlayer. This was interpreted with an energy gap opening induced by the sp^3 enhancement, which was also proved from the density functional calculations. We emphasize that this approach provides a robust means of transforming from metallic (small-gap semiconducting) nanotubes to semiconducting (large-gap semiconducting) ones which is operable at room temperature.

ACKNOWLEDGMENTS

This work was supported in part by the MOST through the NRL and New Frontier programs, and the KOSEF through the CNNC at SKKU. We thank to computer center of Chonbuk National University for the computing resources.

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