Origin of unipolarity in carbon nanotube field effect transistors

Dinh Loc Duong, a Seung Mi Lee b and Young Hee Lee a

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Several mechanisms have been proposed for the origin of unipolar p-type behavior in carbon nanotube (CNT) transistors including (i) O₂ molecules trapped in the metal/CNT contact, (ii) OH radicals on the SiO₂ surface, and (iii) O₂/H₂O coupling on the CNT surface. Nevertheless, the underlying mechanism is far from being clearly understood. Using density functional calculations, we propose that the SiO₂ substrate induces wetting of moisture, which enhances the formation of CNT–OH complexes via several intermediate chemical reactions. As a consequence, the CNT–OH complex provides deep (occupied and unoccupied) acceptor levels near the valence band, acting as an electron trap center, which is the main cause of the asymmetric unipolar behavior of CNT transistors. Based on the theory, I–V characteristics are proposed in terms of gate bias and work function difference between metal and CNTs.

Introduction

In spite of extensive studies on carbon nanotube (CNT)-based field effect transistors (FETs), controlling the carrier type and carrier density is controversial. The initial characteristics of CNT-FETs can be varied from unipolar p-type, n-type to ambipolar behavior, depending on the circumstances. 1–7 Difficulty arises in the presence of adsorbents either on the CNT surface or on the SiO₂ substrate, which is known to be the origin of unipolar p-type transistor behavior. Several mechanisms have been proposed to explain the origin of unipolar behavior. The presence of O₂ at the metal/CNT contact has been proposed to be the main cause of the transitions. 1–3 However, when the SiO₂ substrate is covered by a hydrophobic thin film but the metal/CNT contact is still exposed under ambient conditions, ambipolarity, not p-type unipolarity, is manifested. 5 Naïve contact passivation also demonstrates p-type behavior under humid conditions. 6 Several studies have reported that H₂O in addition to O₂ plays a role in the unipolar p-type behavior. 5,6 The n-type behavior has been observed only under dry air. 7 Several other research groups showed that the p-type unipolar behavior of CNT-FETs is caused by OH-groups on the SiO₂ surface. 9–12 Ambipolar behavior has also been observed under vacuum conditions. 7,8,13 However, the binding of OH-groups on the SiO₂ surface is strong enough not to be desorbed easily under vacuum conditions. 8 Therefore, these two observations are contradictory to each other. Such ambiguity arises from the absence of a microscopic model at the atomic scale.

Recently, the effect of a combined O₂/H₂O ambient environment has been reported in which the combined effect is larger by two orders of magnitude than the individual effects of O₂ or H₂O. 5 Under a humid environment, abundant water molecules are adsorbed on the hydrophilic SiO₂ substrate. As a consequence, the SiO₂ substrate is easily wet, giving rise to H⁺ and OH⁻ ions which enable interactions with CNTs. Protons combined with O₂ molecules extract electrons from CNTs due to the higher reduction potential (by 0.52 eV) compared to that of the CNTs, leaving a charged CNT⁺ state. 5 In this case, the hydrophilic substrate plays a role of wetting H₂O molecules to produce an aqueous environment for these reactions. This is also a well known phenomenon in the chemistry of CNTs in aqueous solutions. 15 Nevertheless, the identity of the final state of the acceptor which suppresses the n branch of CNT-FETs is still not clearly understood.

In this paper, we propose that the CNT–OH complex acts as an electron acceptor. Under O₂/H₂O ambient conditions, the ionized CNT⁺ should be neutralized by OH⁻ in an aqueous solution. By using density functional calculations, we found that the CNT–OH complex creates a deep acceptor level. Band bending associated with the acceptor level provides a clear explanation of unipolar and ambipolar behaviors under different environments and is in excellent agreement with experimental observations.

Calculation methods

The electronic structures of the CNT–OH model were calculated by applying the density functional theory with Perdew–Burke–Ernzerhof generalized gradient approximation (GGA) function for exchange and correlation, as implemented in the Dmol3 package. 16,17 A double numerical plus polarization basis set was used with 4 A orbital cut-off with a 10⁻⁶ Ha convergence threshold for the calculation of the self-consistent energy. A
(10,0) CNT consisting of 240 carbon atoms with a length of 25.56 Å along the z direction was used as a supercell. A large vacuum of 30 Å was added along the x and y directions to eliminate unnecessary interactions with adjacent CNTs as well as OH groups. A gamma point and $1 \times 1 \times 16$ irreducible Monkhorst–Pack $k$-point grid samplings were used for structural relaxation and for calculating the electronic density of states (DOSs), respectively. $\textsuperscript{18}$ The energy convergence was checked using a more refined $1 \times 1 \times 4 k$-point sampling. The energy difference was 1 meV per atom. The structures were fully relaxed until the atomic forces on the atoms were less than 0.002 Ha Å$^{-1}$. The spin calculation of the CNT–OH structure was further checked using the OPENMX code. $\textsuperscript{19}$ The splitting of the spin state was clear from the results of the OPENMX code.

### Results and discussion

#### Trap states of the CNT–OH complex

Fig. 1 shows the band structure of pristine (10,0) CNTs without and with OH groups. The van Hove singularity peaks are visible at the valence and conduction bands. The band gap of (10,0) is nearly 0.9 eV, which is similar to the results of previous reports. $\textsuperscript{20,21}$ Two localized bands are formed near the top valence band in the case of the CNT–OH structure. One band is filled with the up-spin electron and is located 0.2 eV above the top valence band. Another band is empty and is located 0.3 eV above the top valence band. Because of the small difference in the energy between the filled and valence bands, holes can be trapped and detrapped at the filled band. On the contrary, the empty state is far from the conducting band so that an electron can only be trapped. Therefore, asymmetric behavior in the $I$–$V$ characteristics is likely to appear. This clearly shows that adsorbing OH groups on the CNT surface accommodates p-doping by creating hole states at the CNT (lowering the Fermi level to the valence band). The binding energy of OH groups is 1.03 eV, which is sufficiently high not to be desorbed at room temperature.

It is also intriguing to observe the location of trapped electrons. Fig. 2 shows the partial DOS (PDOS) of the CNTs with OH groups. Although both carbon atoms and OH groups contribute to the empty trap state, the contribution of the OH groups is smaller than that of the carbon atoms. To see this effect more clearly, the wave function of the empty band at the gamma point was plotted. The middle and the right panels show the isosurface of the wave function and its cutting plane along the CNTs, respectively. The empty state is mostly localized at OH groups and carbon atoms located at the CNT circumference near the OH sites. This implies that even a single OH bond can effectively screen the transport of electron carriers. This effect will be diminished with large diameter CNTs but the p-doping effect still clearly exists.

In the above model, OH groups are separated by the long distance of the super cell along the tube direction. To see the effect of the concentration of OH groups, we constructed a model of 120 carbon atoms in the super cell, with 12.78 Å along the $z$ direction (half of the value used in the original super cell). $1 \times 1 \times 4$ irreducible Monkhorst–Pack $k$-point sampling was used for structural relaxation. Fig. 3 shows the electronic band structure of the CNT–OH with a high OH concentration. The interactions between the OH groups altered two trap states into new dispersive bands. The up-spin band is half-filled, while the down-spin band is completely empty. This phenomenon is similar to that observed in the highly degenerate semiconductor device with a heavy doping concentration. The responses of CNT-FETs to humidity have been investigated for a long time. However, difficulty remains in understanding the humidity dependence when using a model of charge transfer from H$_2$O molecules to CNTs, where the conductance decreases at a low humidity level and increases at a high humidity level. $\textsuperscript{22,23}$ By using our model, this phenomenon can be understood clearly. In low humidity conditions, the empty acceptor level shown in Fig. 1 is a localized state that acts as a trap center. This localized acceptor increases the scattering of injected hole carriers.
have been used (Table 1). This prediction is supported by the experimental observations in which low metal work function materials such as Al, Ti, and Cr can be observed. In the case of no traps, as summarized in Table 1, in the presence of traps, p-type unipolar characteristics can be observed exclusively, independent of the trap concentration. Yet, due to the work function difference, the conduction band edge is more closely located to the metal work function than the valence band edge. This alters the Schottky barrier height for electrons and therefore the Fermi level shifts of the CNT–OH complex remains stable during the chemical reaction.

Uni-/ambipolar variance of a CNT-FET with different trap state concentrations

Fig. 4 explains the uni-/ambipolar transitions of a CNT-FET with OH groups located on the CNT surface when the work function of the metal electrode is lower than that of the CNTs. Yet, due to the work function difference, the conduction band edge is more closely located to the metal work function than the valence band edge. The Schottky barrier height is increased while that for electron injection. Still, no current is expected at a zero gate bias. At a positive gate bias, the Schottky barrier height is reduced. The band bending is also reduced slightly, as shown in Fig. 4b. No current is expected to flow, similar to other situations. At a negative gate bias, holes can be injected easily into the CNTs due to the low Schottky barrier height, enhancing the hole current unlike in the case of electron injection. Thus, asymmetric ambipolar (higher hole current than electron current) I–V characteristics are expected. This phenomenon has been observed under normal vacuum conditions without severe annealing.

In the case of a high trap density, the Fermi level is further downshifted to the top of the valence band. At a zero gate bias, there is no current to flow, similar to other situations. At a positive gate bias, electrons injected into the CNT channel can be trapped by the empty trap sites, further reducing the current compared to the no trap case. Holes can be injected easily into the CNTs at a negative gate bias due to the low Schottky barrier height, enhancing the hole current unlike in the case of electron injection. Therefore, p-type unipolar characteristics are expected. This is consistent with experimental observations. A similar operation principle can be applied when the work function of the metal electrode is larger than that of the CNTs. The band bends upward in this case (figure not shown) and no n-type characteristics can be observed in which low metal work function materials such as Al, Ti, and Cr have been used. In the case of the low trap density, the Fermi is slightly downshifted due to the presence of trap sites near the valence band edge. This alters the Schottky barrier height for electrons and reducing the conductance. On the other hand, at high humidity, this state is dispersive or delocalized due to their interactions and contributes to the hole state, therefore increasing the conductivity of the device.

The chemical potential of the combined O₂/H₂O system strongly relies on the pH of the environment, which varies from -5.66 to -4.83 eV. The Fermi level shifts of the CNT–OH structures with small and high OH concentrations are 0.25 and 0.45 eV, respectively, which are located below the chemical potential of the pure CNTs but still within the chemical window of the reaction. This implies that the electrons generated from the CNTs during the H⁺/OH⁻ reaction can be easily transferred to the system, which facilitates the necessary chemical reaction and therefore, the CNT–OH complex remains stable during the chemical reaction.
the CNTs. In our theoretical approach, two densities of OH groups were used. The concentration of OH groups with (10,0) CNTs in the low density limit was estimated as $5 \times 10^{13}$ cm$^{-2}$. In the high density limit, the trap density was increased by a factor of two and empty trap states were still observed, as shown in Fig. 3. The carrier concentration in a FET device is approximately $10^{13}$ cm$^{-2}$. This value is also comparable to the OH concentration of $7 \times 10^{13}$ cm$^{-2}$ on the SiO$_2$ surface. Experimentally, p-type unipolar characteristics were observed, congruent with our theoretical predictions. This implies that the electron density cannot exceed the trap density in the CNT channel under normal experimental conditions.

**Conclusion**

In summary, we proposed the origin of uniaxial bipolar behavior of CNT-FETs under various trap densities and work functions of the metal electrodes. The main origin of the underlying mechanism in determining the polarity of CNT-FETs is the empty trap states from the CNT–OH complex. By taking into account the metal work function and trap density, our theory based on the band bending diagram provides a comprehensive analysis for all possible unipolar n-type and p-type characteristics as well as ambipolar characteristics in the CNT-FET devices and is in excellent agreement with the experimental observations. The chemical reaction route in forming the CNT–OH complex was also clarified.

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**Notes and references**


19 http://www.openmx-square.org/


