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Electronic structure of single-walled carbon nanotubes on ultrathin insulating films

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The electronic structures of single-walled carbon nanotubes on Ag(100) and on ultrathin insulating NaCl(100)/Ag(100) were studied using low-temperature scanning tunneling microscopy. The Fermi level of the nanotubes was shifted toward the conduction band on Ag(100), while it was shifted toward the valence band on NaCl films. We explain this opposite behavior by different basic mechanisms accounting for the Fermi level shifts. On the metal surface, the work function difference between the tube and the substrate determines the direction of the Fermi level shift. In the case of carbon nanotubes on insulating films, the electric field resulting from the dipole moment formed at the interface between the insulating film and the metal plays a decisive role in determining the Fermi level. © *2008 American Institute of Physics.* [DOI: 10.1063/1.3046114]

Single-walled carbon nanotubes (SWCNTs) are undoubtedly one of the most promising materials for future development of nanoscale electronic devices.[1,2] To make such devices possible, it is necessary to acquire a detailed understanding on the behavior of a SWCNT in contact with various materials. Low-temperature scanning tunneling microscopy (LT-STM) and scanning tunneling spectroscopy (STS) are especially well suited to studying local electronic structures with atomic resolution.[3–5] Most experiments on SWCNT devices have been carried out on insulating layers for practical applications; to date, however, STM studies have been restricted to SWCNTs on metals[3–5] or semiconductors.[6,7] In the case of insulating films of only a few atomic layers in thickness, electrons can tunnel through the film while the hybridization that takes place between a molecular adsorbate and a conducting substrate could be substantially reduced for STM study.[8–10] However, due to the difficulties in preparing SWCNTs on insulating films in the extremely clean conditions required for STM study in ultrahigh vacuum (UHV) environment, the electronic structure of SWCNTs on insulating films has not yet been a focus of study. In this letter, we report on our study of the electronic structure of SWCNTs on NaCl(100)/Ag(100) by STM and STS. We were able to prepare SWCNTs by employing a dry contact transfer (DCT) technique, a method for depositing SWCNTs on various kinds of substrates.[6,7,11] Our results show the importance of the substrate on the electronic structure of SWCNTs, especially the Fermi level (E_F) alignment. With regard to the opposite behavior observed, we discuss on the origin of the E_F shift on metal substrate and on insulating film.

The experiments were carried out in an UHV low-temperature scanning tunneling microscope (Omicron LT-STM) at 4.7 K. The Ag(100) single crystal was cleaned by several cycles of sputtering and annealing. After sample cleaning, the NaCl film was deposited on the substrate by thermal evaporation at 600 K. Finally, HiPCO SWCNTs (Carbon Nanotechnologies, Inc.) were deposited *in situ* by the DCT method on the NaCl/Ag(100) substrate in an UHV chamber.[11] By this method, we were able to prepare SWCNTs on the NaCl/Ag(100) surface without significant contamination of the samples. In our STM results, all the bias voltage refers to the sample voltage with respect to the tip.

Figure 1(a) shows the NaCl islands on the Ag substrate. The NaCl islands grow in the carpet growth mode on Ag(100). In general, the nucleation of NaCl begins from the step site and spreads over both terraces. Figures 1(b) and 1(c) show SWCNTs deposited on the NaCl films. Isolated SWCNTs were easily found elsewhere on NaCl islands or on silver by means of STM. In some cases, SWCNTs were placed both on the Ag substrate and on the NaCl islands as in Fig. 1(c), where the left side of the tube was positioned over the silver and the right side was placed on NaCl layers of 2 ML in thickness.

In order to investigate the electronic structure of SWCNTs, we measured differential conductance, dI/dV, of SWCNTs on Ag(100) and on NaCl(100) films, respectively. The dI/dV was obtained with a lock-in detection by applying a modulation of 50 mV (rms) to the tunneling voltage at 797 Hz. The E_F of the SWCNTs on Ag(100) shifts toward the conduction band (CB), that is, the midgap position is located from about −500 to −100 meV [Figs. 2(a)–2(c)]. In contrast, the position of E_F shifts to the valence band (VB) on the NaCl film, where the midgap of the SWCNT is located at about +300 − +400 meV [Figs. 2(d)–2(f)]. Regardless of the type of the tubes (semiconducting or metallic), the E_F shifts in all SWCNTs were similar to the above results (toward the CB on the silver and toward the VB on the NaCl films). The E_F shift toward the VB direction has been reported in many STS studies on SWCNTs on the Au(111) surface.[3] The most important factor determining the position

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FIG. 2. (Color online) The dI/dV spectra recorded on various SWCNTs: [(a)–(c)] on Ag(100) and [(d)–(f)] on NaCl/Ag(100). The vertical dashed lines indicate the location of E_F.
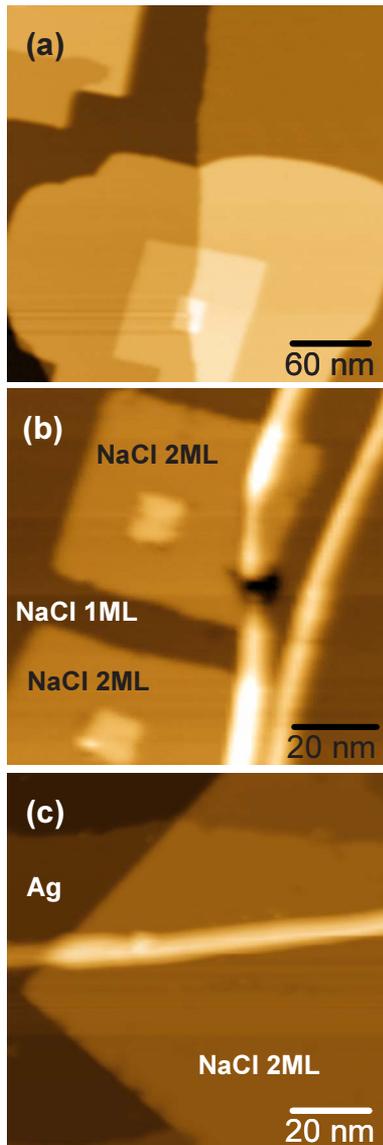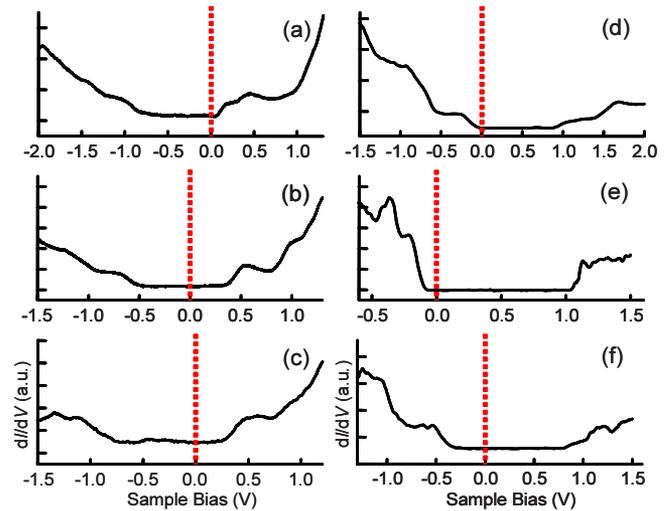

FIG. 1. (Color online) (a) STM image of NaCl(100) islands on the Ag(100). [(b) and (c)] STM images of SWCNTs on the NaCl islands and Ag substrate. The imaging conditions are (a) V_S=1.5 V and I_T=250 pA, (b) V_S=3.5 V and I_T=250 pA, and (c) V_S=1.5 V and I_T=250 pA, respectively.

the electron affinity of the SWCNTs, so those having different chiralities or different adsorption geometries can have a different degree of VL shift on Ag(100).

The WF of the surface changes when an insulating film is deposited on the metal surface. In the case of Ag(100), the WF is reduced to about 3.6–4.0 eV by deposition of a NaCl film.[19] If we consider only the WF values of the tube and the NaCl films, the E_F of a SWCNT should be shifted much more to the CB. However, the direction of E_F shift for the SWCNTs on NaCl in the experimental results was the opposite, i.e., to the VB. This means that the different WFs between SWCNT and substrate are not the dominant factors for determining the E_F shift in this case.

What is the driving force of the E_F shift in SWCNTs on an insulating film? The dipole moment at the interface seems likely to be responsible. When an insulating film interfaces with a metal surface, interface states, i.e., metal-induced gap states (MIGSs), develop at the interface.[20,21] The presence of MIGS at the interface gives rise to a charge transfer across the interface, creating a dipole moment. The substrate-induced polarization of electrons in metal is also a reason for the interfacial dipole moment. In the case of NaCl/Ag(100),

of E_F of a SWCNT on the metal substrate is the difference in work functions (WFs) between the tube and the substrate.[12,13] This means that the charge transfer between the SWCNT and the metal substrate can be varied according to the WFs of the substrates. Since the WF of Ag(100) is about 4.4 eV,[14] which is smaller than that of Au(111) (5.3 eV),[15] the charge transfer occurs from the SWCNT to the Ag(100) and from the Au(111) to the SWCNT, which is known to have a WF around 4.8 eV.[16,17] However, the difference in WF between SWCNTs and a substrate is not sufficient to explain quantitatively the E_F shift shown in the present work. Organic/metal interfaces manifest an interfacial dipole layer due to charge transfer, image charge formation, chemical interaction, interfacial state, and other factors.[18] Since the chemical potential of electrons is much higher in silver than in the SWCNTs, electrons flow from Ag to a SWCNT to achieve equilibrium at the interface (Fig. 3). As a result, interfacial dipole moments are generated and the E_F alignment shifts. The vacuum level (VL) shift depends on
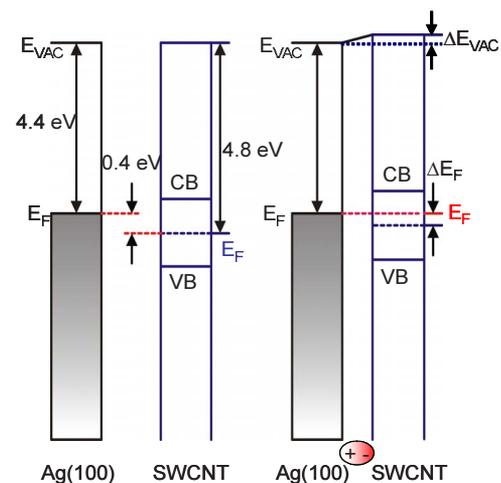

FIG. 3. (Color online) Schematic of interfacial energy of SWCNT/Ag(100) before (left) and after (right) contact.
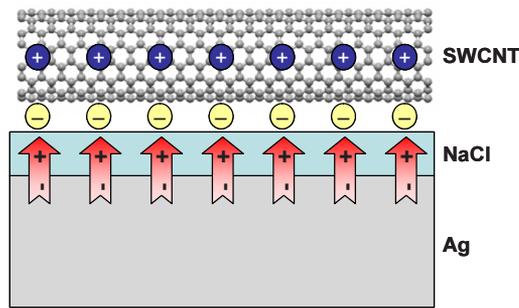
FIG. 4. (Color online) Schematic of a SWCNT on NaCl/Ag(100) showing the dipole moments at the interface and their role in attracting electrons from the SWCNT.

the calculated results in Ref. 19 also revealed that an interfacial dipole moment developed at the interface due to an electron depletion in the insulating film in favor of the substrate. The direction of the electric field created in this way attracts electrons from the SWCNT to the substrate, which ultimately results in effective *p*-doping of the tube (Fig. 4). We believe that the effect of the dipole moment is not negligible on ultrathin insulating films and that this is the reason why the E_F shift in the tube on the NaCl film is opposite to that on Ag(100) in spite of the lowered WF of the substrate. Since the electric field of interfacial dipole moment varies according to the thickness of the insulating film,[21] we could expect that this might also affect the E_F alignment of the SWCNTs. However, we could not compare the amount of the E_F shift as a function of the thickness of the NaCl layers from our data. Most of our STS data were measured from the SWCNTs on the NaCl films of 1 or 2 ML in thickness; for example, the STS data in Figs. 2(d)–2(f) were measured from the SWCNTs on the different NaCl films of the same thickness (2 ML). Depending on the SWCNTs, the E_F of the tubes even on the NaCl films of the same thickness are distributed in a wide range as those on the silver substrate. So it is difficult to directly correlate the E_F shift in various SWCNTs with the thickness of the NaCl layers from the current STS data.

To summarize, we examined the E_F alignment of SWCNTs on Ag(100) and ultrathin NaCl films by means of LT-STM and STS. On pristine metal surface, the E_F shift was influenced by the difference in the WFs of substrate and the nanotube, whereas the electric field created at the interface between the insulating NaCl film and the metal substrate was decisive in determining the E_F of the SWCNT on the NaCl

film. It is well known that the doping of SWCNTs is not easily achieved by conventional semiconductor processes such as ion implantation or chemical modification. Our results suggest one way of controlling the E_F of SWCNTs and also reveal the importance of the nanometer-scale insulating layer in determining the E_F alignment not only for SWCNTs but also for other kinds of molecular systems on insulating film.

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