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Controllable modification of transport properties of single-walled carbon nanotube field effect transistors with *in situ* Al decoration

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We use an *in situ* Al decoration technique to control the transport characteristics of single-walled carbon nanotube field effect transistors (SWNT-FETs). Al nanoparticle decoration in a high vacuum caused the devices to change from *p*-type to *n*-type FETs, and subsequent exposure to the ambient atmosphere induced a gradual recovery of *p*-type character. In comparison with the bare SWNT-FETs under high vacuum, the channel-open devices with decorated Al particles exhibited reduced current under ambient conditions. However, selective Al decoration only at the contact resulted in an improved *p*-type current in ambient air. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2798590]

Single-walled carbon nanotubes (SWNTs) have been extensively studied due to their potential applications in electronic devices such as transistors, diodes, logic gates and sensors.[1] However, several key issues need to be addressed before SWNTs can be successfully implemented in electronics. In the field of nanotube-based devices, the fabrication of high-performance and air-stable *n*-type transistors is one of the greatest challenges. To achieve this objective, electron doping in the SWNT channel has been tried using alkali metals such as potassium[2] or amine-rich polymers.[3,4] On the other hand, low work function metals such as Ca or Al have been employed to lower the Schottky barrier for electron transport at the contact.[5,6]

In the present study, we fabricated *n*-type SWNT-FETs using a controlled *in situ* Al nanoparticle decoration technique. In order to compare the contribution from the Schottky barrier modification with that from the carrier density change in the channel, we used three device configurations: channel-covered (contact-open), contact-covered (channel-open), and all-open devices. All devices showed *p*-type character under a high vacuum prior to Al decoration. After Al decoration, the devices turned into *n*-type FETs and recovered the *p*-type character again after exposure to ambient air.

The SWNT-FETs used in this research were fabricated by a patterned catalyst growth technique,[7] followed by photolithography and metallization. Electrode patterns were made with photolithography, and 5 nm Ti and 20 nm Au were evaporated successively using thermal evaporation. Before the Al decoration, our device showed clear *p*-type behaviors even in high vacuum. This indicates that the bilayer metal electrode provided a partial contact between carbon nanotube (CNT) and the gold layer, especially at the edge of the electrode. It is also reported that only a few overlaying metal monolayers are enough to change the work function of bimetal system to that of surface metal.[8] In this regard, the overall work function of the Ti/Au electrodes could substantially differ from that of pure Ti layer and be close to that of Au overlaying metal (~5.2 eV). In addition to the bare SWNT-FET (open device), contact-covered and channel-decorated SWNT-FETs were prepared using SU8-2002 negative photoresist or polymethyl methacrylate masks.

For Al decoration, the vacuum chamber was pumped down below 2×10^{-6} torr. Removal of oxygen from the device during pumping decreased the hole concentration and lowered a work function of metal electrode slightly, weakening the *p*-type characteristics. Al source was slowly evaporated thermally while monitoring the conductance from SWNT-FETs. Figure 1(a) shows the change of gate response characteristics measured from a SWNT-FET during controlled Al deposition. During Al deposition, the gate transfer curves shift toward negative gate voltages. Inspection of the curves in Fig. 1(a), which were taken at 10 s intervals, shows

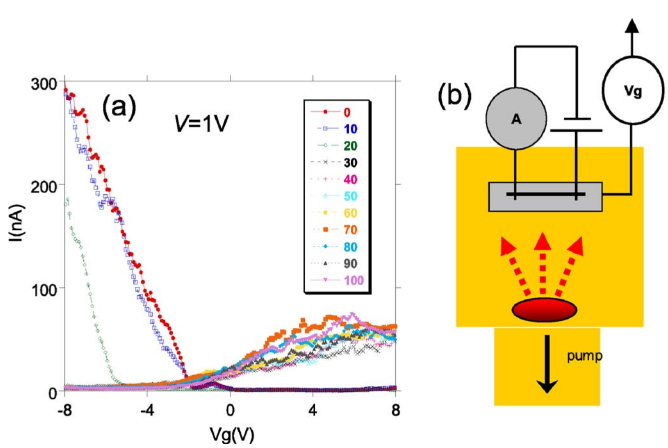

FIG. 1. (Color online) (a) The evolution of electronic transfer characteristics upon Al decoration. The curves were recorded at 10 s intervals. (b) Schematic diagram of the measurement setup.

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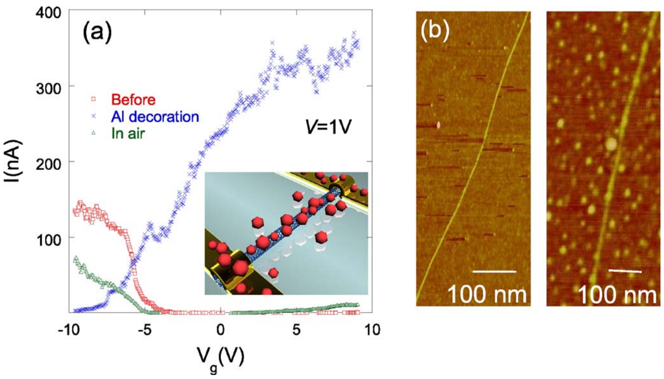

FIG. 2. (Color online) (a) The gate response curves of the open SWNT-FET before and after Al deposition under vacuum and after exposure to ambient air, respectively. The inset shows a schematic diagram of the Al-decorated SWNT-FET. (b) AFM images of the nanotube before and after Al decoration.

that the *p*-type conduction had disappeared completely after about 30 s. The deposition rate was carefully controlled to <0.1 Å/s. After around 40 s of deposition, a *p*-type SWNT-FET turned into a *n*-type SWNT-FET, as shown in Fig. 1.

Figure 2 shows the gate response characteristics and atomic force microscopy (AFM) images of the open SWNT-FET before and after Al deposition. For this sample, a nominal 20-Å-thick Al layer was deposited while monitoring the conductance. As shown in Fig. 2(a), the *n*-branch current after the Al deposition is about three times larger than the *p*-branch current before the deposition. The deposited Al nanoparticles are spread out over the open SWNT-FET device, as shown in Fig. 2(b). The Al nanoparticles adsorbed on the surface of the carbon nanotube must have induced electron doping in the nanotube channel. Since the work function of Al (~4.1 eV) is lower than that of the nanotube (~4.8 eV),[9,10] electron transfer must occur from the Al particles to the nanotubes. In addition, the Al clusters adsorbed at the contact region may also contribute to the *n*-type transport by lowering the Schottky barrier height.[9,11] However, when the device was exposed to ambient air after Al decoration, the device gradually recovered its *p*-type behavior. This phenomenon has been attributed to the oxidation of Al particles on the channel regions as well as the contact regions.[12] Here, however, we observe that the recovery of the *p*-branch current is incomplete and the threshold voltage is slightly more negative than that of the bare device.

To obtain a detailed understanding of the effects of Al decoration, we tried to separate the effect of the contact barrier adjustment from that of channel doping. Here, we first consider the contact-covered device. Figure 3 shows the gate response characteristics of the contact-covered device before and after Al decoration under vacuum and after subsequent exposure to ambient air. As shown in Fig. 3(a), the device transforms into a *n*-type FET after Al decoration. In this case, however, the *n*-branch current is rather small and the threshold voltage is more positive in comparison with the open device, as discussed above. This can be attributed to the fact that the contact barrier of the contact-covered device is unaffected by the adsorption. The open device, as discussed above, has two components which contribute to the *n*-type operation: the lowering of the Schottky barrier and electron doping in the channel. The contact-covered device, by contrast, has contributions only from the second of these components, and hence the *n*-branch current is small in comparison with that of the open device.

After exposure to ambient air, the Al-decorated channel-open device recovers its *p*-type character although not completely. The *p*-branch current level is lower than that of the bare device and the gate threshold remains at a more negative position (about −4 V). Note that the open SWNT-FET as mentioned previously had similar features. The recovery of *p*-type character can be explained by the oxidation of Al particles.[10] The oxidized Al surface has a work function as large as that of gold and could accept electrons from SWNTs. In this regard, the incomplete recovery of the *p*-type character of the FET, shown in Fig. 3(a), may indicate that the Al particles are oxidized only partially. However, we cannot rule out the possibility that the irreversible bond formation occurs between the deposited Al and the SWNTs or that the oxygen is chemisorbed on the nanotube surface. In addition to the above mentioned effects, the surface-bound oxidized Al particles can behave as scattering centers for electronic conduction, which may have caused the observed reduction of the conductance.[12] In addition, the presence of oxidized Al layers may have hindered the adsorption of oxygen on the

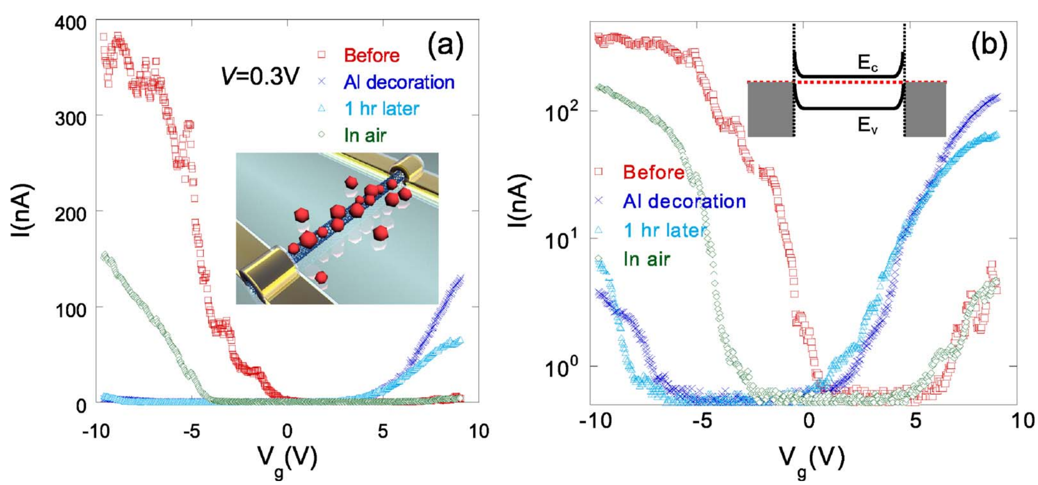

FIG. 3. (Color online) (a) The transfer characteristics of the contact-covered SWNT-FET before and after Al deposition, 1 h later under vacuum, and after exposure to air for 10 min, respectively. The inset shows a schematic diagram of the device. (b) Log-scale plot of electrical transfer characteristics of the channel-decorated SWNT-FET. The inset shows the schematic band diagram of the electron-doped *n*-type nanotube transistor.

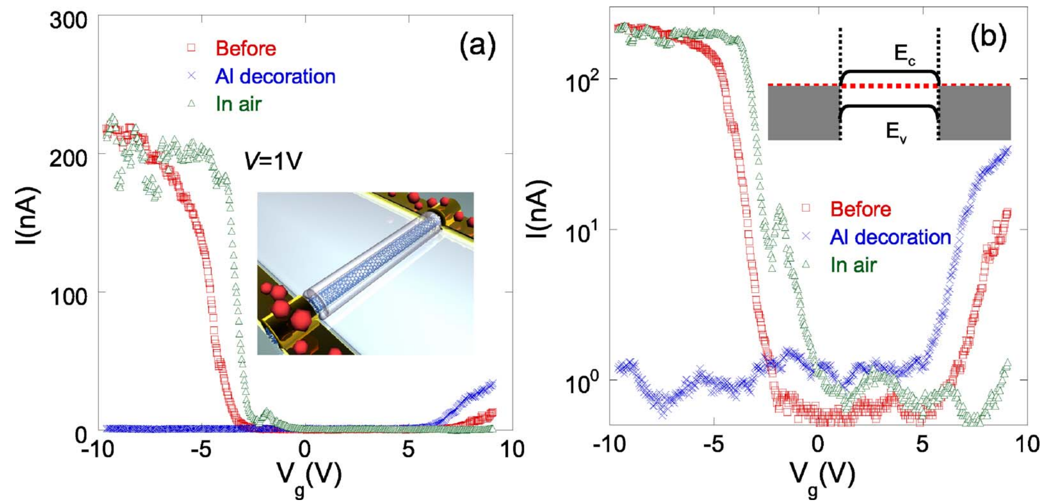

FIG. 4. (Color online) (a) The transfer characteristics of a channel-covered SWNT-FET before and after the Al deposition under vacuum and after exposure to air, respectively. The inset shows a schematic diagram of the device. (b) Log-scale plot of the electrical transfer characteristics of the channel-covered SWNT-FET. The inset shows a schematic band diagram of the SWNT-FET with a lower electron Schottky barrier.

SWNT surface. Figure 3(b) shows a log-scale plot of the electrical transfer characteristics along with a schematic band diagram of the electron-doped *n*-type nanotube transistor.

We now turn to the channel-covered device, as shown in Fig. 4. Similar to the channel-open devices, the SWNT-FET with covered channels also showed *p*-type transport behavior under vacuum and changed into a *n*-type FET after Al decoration. The change to *n*-type behavior in this case should be attributed to the lowering of the Schottky barrier for electron transport. In a high vacuum, the adsorption of oxygen molecules on the sidewalls of the nanotube is believed to be minimal,[13] and since the work function of Al is low, the Fermi level of the Al-decorated electrode will line up with the conduction band edge of the SWNT.[10] However, in marked contrast to the channel-open devices, the contact-decorated channel-covered device completely recovered the *p*-type conductance of the bare device after exposure to ambient air. Moreover, as shown in Fig. 4(a), the subthreshold swing S of the device after exposure to air (0.6 V/decade) is slightly improved compared to that of the *p*-type SWNT-FET before Al decoration in a vacuum (about 1.2 V/decade). Such a behavior is consistent with our previous findings that highly improved sensor performance can be obtained with Al-decorated SWNT-FETs.[14]

The full recovery of *p*-type character indicates that the Al nanoparticles at the contact region were fully oxidized. It was found that the Fermi level of an oxidized Al surface lines up with the valence band edge of the nanotube.[10] This provides further support for the hypothesis, as discussed previously, that the incomplete recovery of the *p*-type character of the channel-open devices is more likely to be due to the formation of Al-CNT chemical bonds or irreversible chemisorption of oxygen on the SWNT surface.

In summary, we have shown that the transport characteristics of SWNT-FETs can be modified through an *in situ* Al decoration technique. Al decoration under vacuum caused the device to change from a *p*-type to a *n*-type transistor and the original *p*-type character was recovered following exposure of the decorated device to the ambient atmosphere. In contrast to the channel-open devices, the devices with Al particles only at the contact showed improved transistor performance after exposure to ambient air. These findings suggest that oxygen adsorption on the Al-decorated SWNT channel region gives rise to a permanent decrease of the conductance, whereas the contact barrier is fully recyclable over the process of Al decoration and subsequent oxygen adsorption.

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