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Air-stable *n*-type operation of Gd-contacted carbon nanotube field effect transistors

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We report air-stable *n*-type operations of the single-walled carbon nanotube field effect transistors (SWNT-FETs) fabricated with Gd electrodes. Unlike previously reported *n*-type SWNT-FETs, our devices maintained their *n*-type operation characteristics in ambient atmosphere for more than two months. The shallow Gd films with a thickness below 20 nm are corroded by environmental oxygen, whereas the well-contacted Gd-SWNT interfaces underneath the thick Gd layers are protected from contaminations by air molecules. Theoretical studies based on the first-principles electronic structure calculations confirm that Gd layers have an excellent binding affinity to the SWNTs.

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Electronic devices based on molecular building blocks have attracted increasing interest because they may provide solutions for keeping track of Moore's law. Since molecular structures are not limited by lithography resolution, they could allow a further reduction in the chip size compared to patterned devices.¹ Among the various molecular switching units suggested or tested to date, single-walled carbon nanotube (SWNT) is an exemplary case due to its excellent electronic properties, which include an exceptional current-carrying capacity and a high mobility.^{2,3} Several research groups have reported the successful fabrications of SWNT-based diodes,⁴⁻⁶ logic gates,^{7,8} and chemical⁹ or biological sensors.^{10,11} Nevertheless, a few key technological issues still remain challenging, for example, the fabrication of *n*-type SWNT-field effect transistors (FETs) is necessary for the complementary logic circuits. SWNT-FET, without a special treatment, normally tends to show *p*-type behavior, which is attributed to either Fermi-level alignment at the contact or hole doping in the channel by environmental oxygen species, including water vapors and oxygen molecules.^{12,13}

The existing strategies for fabricating *n*-type SWNT-FETs can be classified into two categories. In the first approach, electron dopants such as alkali metals or polymers are employed to generate electron carriers in the body of the SWNTs.^{14,15} The second approach entails engineering the contact barrier to achieve a lower Schottky barrier for electron transport into the conduction bands of the SWNTs. Nevertheless, in practice, electron dopants are vulnerable to oxidation and the work function of the metal surface is likely to increase upon oxidation under ambient air.¹⁶ Therefore, irrespective of the method used (channel doping or the contact-barrier engineering), achieving long-term stability of *n*-type operation under ambient conditions remains a great challenge. Shim *et al.*¹⁵ demonstrated that polyethyleneimine-coated SWNTs could lead to air-stable *n*-type transistor operations and Zhang *et al.*⁸ achieved the same objective by

following the second route. They reported the fabrication of the SWNT complementary devices and showed that Sc-contacted SWNT-FETs appear to exhibit a long-term air-stable *n*-type behavior without passivation.⁸

In this work we fabricate Gd-contacted SWNT-FETs, noting that the work function of Gd (~ 3.1 eV) is much lower than that of carbon nanotube (~ 4.8 eV). Unlike other low-work-function elements, Gd is relatively stable in dry air¹⁷ and also widely used for electronic and medical applications. We report that the *n*-type behavior of the Gd-contacted SWNT devices is maintained for more than two months in air. To prepare the devices, SWNTs were grown on heavily doped *p*-Si wafers covered by 500 nm thick SiO₂ insulating layer. Details of the device fabrication procedure are described elsewhere.¹⁶ We deposited the Gd layer by means of *e*-beam evaporation. Figure 1 shows the electrical transport characteristics of a SWNT-FET, contacted with 50 nm thick Gd electrodes after 50 days of air exposure. The length and diameter of the channel are 5 μm and 2.5 nm, respectively. The device shows clear *n*-type transport in ambient atmosphere, and an electron mobility goes up to 811 cm²/V s.¹⁸ Moreover, the on/off ratio is larger than 5×10^5 ($I_{\text{on}}=0.926$ μA and $I_{\text{off}}=1.6$ pA at $V_{\text{sd}}=300$ mV).

We also characterized the device under high vacuum conditions (below 10^{-6} torr) to minimize the effects of environmental oxygen. Figure 1(b) shows a semilogarithmic plot of the electrical conductance of a Gd-contacted SWNT in air (red) and vacuum (blue). The gate threshold voltage shifts toward negative direction upon evacuation, and a small increase in the on-state current is observed. Such a negative shift in the gate threshold voltage is attributed to the depletion of hole carriers, which is accompanied by desorption of oxygen species. The shift in the gate threshold voltage upon evacuation ($\Delta V_g \sim 3.4$ V) is almost the same for all the tested devices with similar channel lengths of about 5 μm . The amount of charge transferred from environmental oxygen species estimated from $\Delta n \approx C_g \Delta V_{\text{th}}/eL$ is about 0.7 electrons/nm. Considering that a physisorbed oxygen mol-

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FIG. 1. (Color online) Electrical transport characteristics of a SWNT-FET contacted with a 50 nm thick Gd electrodes. (a) Gate-dependent conductance (I - V_g) measured using the bias voltages between 0.06 and 0.3 V. Inset: atomic force microscopy image of the device; the scale bar is 1 μm . (b) Semilogarithmic plot of I - V_g measured in vacuum (blue) and in air (red) with a bias of 0.3 V. Inset: a schematic diagram of the device.

ecule withdraws only a few hundredths of an electron from the nanotube,¹⁹ the observed shift in the gate threshold may roughly indicate that several oxygen molecules per nanometer are adsorbed on the nanotube surface.

Now we investigate the long-term stability of the n -type feature of our SWNT-FETs at various thicknesses of the Gd layer. Time evolutions of the electrical transport properties of SWNT-FETs with 50 nm thick Gd electrodes are presented in Fig. 2(a). Although Fig. 2(a) shows relatively large shifts in the threshold voltages and the reduced on/off ratio versus time both for vacuum and air, it is noteworthy that the n -type features of the devices persisted for more than two months. Previously, researchers tried to preserve the n -type behavior of the SWNT-FETs by protecting the metal contact from oxidation, thereby utilizing polymers²⁰ or a Si_3N_4 membrane.²¹ Here we do not use any protection layers. We only note that the long-term stability is strongly related to the thickness of the Gd layer. Figure 2(b) shows the I - V_g characteristics of a SWNT-FET contacted with a 10 nm thick Gd layer. Immediately after being fabricated, the device showed n -type transistor behavior. However, both the p - and n -channel currents decreased substantially as time elapsed.

Upon increasing the Gd film thickness to 20 nm, one-third of the device showed a large decrease in the conductance or instability, whereas the other two-thirds showed only minor changes caused by aging in the ambient atmo-

sphere. In contrast, all the devices contacted with Gd films thicker than 30 nm were stable for over two months. Based on these results we believe that the Gd surface has a strong binding affinity with SWNT surfaces, and thus the environmental oxygen molecules did not penetrate into the Gd-SWNT surface. On the other hand, since the Gd layer itself is vulnerable to oxidation, a shallow Gd layer is likely to be completely eroded, providing a highly resistive contact. It appears that a Gd layer with a minimum thickness is required to obtain a stable n -type SWNT-FET.

Another extraordinary feature of our SWNT-FETs with thick Gd contacts is the substantial negative shift in the I - V_g curve with the aging in ambient air, as shown in Fig. 2(a), which is in obvious contrast to usual SWNT-FETs. We conjecture that the strong binding affinity of the Gd layer with the SWNT is likely to lead to a spontaneous improvement in the contact. The contaminants initially located at the Gd-SWNT interface will gradually diffuse away with the long-time aging process, resulting in the negative shift in the I - V_g . On the other hand, the adsorptions on the SWNT body induce hole doping, giving rise to the positive shift in the I - V_g curve. We also note that the vacuum of 10^{-6} Torr is not an extremely high vacuum, and thus the long-time exposure may lead to a substantial adsorption. The observed modest positive shift in the I - V_g under the vacuum condition is believed to be the outcome of the interplay between the two

FIG. 2. (Color online) Long-term stability of Gd-contacted SWNT-FET. The source-drain bias voltage (V_{sd}) was 0.1 V. (a) Semilogarithmic plot of the conductance of a SWNT-FET with 50 nm thick Gd electrodes in air (blue and red curves) and in vacuum (green and gray curves). (b) Semilogarithmic plot of the conductance measured from the SWNT-FET with 10 nm thick Gd electrodes.

FIG. 3. (Color online) Optimized geometry of the (10, 0) carbon nanotube in contact with three layers of (a) Gd and (b) Al.

opposing mechanisms: negative shift by the contact aging and positive shift by the adsorptions on the CNT body.

To understand the observed long-term stability of the *n*-type feature of our Gd-contacted SWNT-FETs, we perform the density-functional-theory-based first-principles calculations of SWNTs in contact with various metal surfaces. We use the Vienna *Ab initio* simulation package, and the projected augmented wave potential and the generalized gradient approximation are selected for this calculation.²² We are particularly interested in the binding affinity of the SWNT to the Gd surface in comparison to a known metal surface such as Al. Figures 3(a) and 3(b) show optimized geometries of the SWNT in contact with three layers of Gd and Al, respectively. We first optimized the bulk structures of Gd and Al in the hexagonal close packed and face-centered cubic lattices, respectively. Then, three layers of Gd and Al were constructed assuming the same bond length as that of the bulk crystal, and a side contact to the SWNTs was introduced, as shown in Fig. 3. In accordance with our conjecture proposed in previous paragraphs, the Gd surface exhibits a strong binding affinity to the SWNTs. This is not the case for the Al layers with (111) surface. In the optimized geometry, the SWNT is separated from the Al surface by the van der Waals distance. Both Al and Gd have lower work functions than the SWNTs. Therefore both metals can act as electron donors, thus inducing a *n*-type operation in the SWNT-FETs.¹⁶ However, the air stability of the *n*-type behavior of Gd-based devices is characteristically different from that of Al-based devices, which is mainly attributed to the differences in surface chemistry.

In summary, we fabricated Gd-contacted SWNT-FETs and found that the *n*-type characteristics of the devices were exceptionally stable under ambient air. SWNT-FETs composed of Gd electrodes with a thickness above 30 nm maintained their *n*-type behavior for more than two months under ambient air conditions, whereas the conductance of devices with thin Gd electrodes degraded substantially within a few

days. We attribute this behavior to the strong binding affinity of the Gd layers to the SWNTs in conjunction with the strong oxidation tendency of the Gd surfaces and suggest that Gd contacts with an appropriate thickness could be a very practical solution for obtaining the air-stable *n*-type SWNT-FETs.

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¹K. S. Kwok and J. C. Ellenbogen, *Mater. Today* **5**, 28 (2002).

²B. Q. Wei, R. Vajtai, and P. M. Ajayan, *Appl. Phys. Lett.* **79**, 1172 (2001).

³T. Durkop, S. A. Getty, E. Cobas, and M. S. Fuhrer, *Nano Lett.* **4**, 35 (2004).

⁴Y. Noshu, Y. Ohno, S. Kishimoto, and T. Mizutani, *Appl. Phys. Lett.* **86**, 073105 (2005).

⁵C. Lu, L. An, Q. Fu, H. Zhang, J. Murduck, and J. Liu, *Appl. Phys. Lett.* **88**, 133501 (2006).

⁶B.-K. Kim, J.-J. Kim, N. Park, H.-M. So, K. Kong, H. Chang, and J.-O. Lee, *Appl. Phys. Lett.* **89**, 243115 (2006).

⁷A. Bachtold, P. Hadley, T. Nakanishi, and C. Dekker, *Science* **294**, 1317 (2001).

⁸Z. Zhang, X. Liang, S. Wang, K. Yao, Y. Hu, Y. Zhu, Q. Chen, W. Zhou, Y. Li, Y. Yao, J. Zhang, and L.-M. Peng, *Nano Lett.* **7**, 3603 (2007).

⁹J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, and H. Dai, *Science* **287**, 622 (2000).

¹⁰H.-M. So, K. Won, Y. H. Kim, B.-K. Kim, B. H. Ryu, P. S. Na, H. Kim, and J.-O. Lee, *J. Am. Chem. Soc.* **127**, 11906 (2005).

¹¹H.-M. So, D.-W. Park, E.-K. Jeon, Y.-H. Kim, B. S. Kim, C.-K. Lee, S. Y. Choi, S. C. Kim, H. Chang, and J.-O. Lee, *Small* **4**, 197 (2008).

¹²S. J. Tans, A. R. M. Verschuere, and C. Dekker, *Nature (London)* **393**, 49 (1998); N. Park and S. Hong, *Phys. Rev. B* **72**, 045408 (2005).

¹³P. G. Collins, K. Bradley, M. Ishigami, and A. Zettl, *Science* **287**, 1801 (2000).

¹⁴C. Zhou, J. Kong, E. Yenilmez, and H. Dai, *Science* **290**, 1552 (2000).

¹⁵M. Shim, A. Javey, N. W. S. Kam, and H. Dai, *J. Am. Chem. Soc.* **123**, 11512 (2001).

¹⁶H.-S. Kim, B.-K. Kim, J.-J. Kim, J.-O. Lee, and N. Park, *Appl. Phys. Lett.* **91**, 153113 (2007).

¹⁷D. E. Eastman, *Phys. Rev. B* **2**, 1 (1970).

¹⁸We modeled the system as a cylinder on an infinite plane. The gate capacitance can be derived as $C_g = 2\pi\epsilon\epsilon_0 L / \ln(h/r)$, where the length of the channel (L) is 5 μm , the radius of SWNT (r) is 1.2 nm, and gate oxide thickness (h) is 500 nm. Since the transconductance of the device at $V_{sd} = 0.3$ V is found to be $dI/dV_g = 0.175 \mu\text{S}$, the mobility is $\mu = (dI/dV_g)(L^2/C_g V) = 811 \text{ cm}^2/\text{V s}$.

¹⁹P. Giannozzi, R. Car, and G. Scoles, *J. Chem. Phys.* **118**, 1003 (2003).

²⁰V. Derycke, R. Martel, J. Appenzeller, and Ph. Avouris, *Nano Lett.* **1**, 453 (2001).

²¹D. Kaminishi, H. Ozaki, Y. Ohno, K. Maehashi, Y. Seri, A. Masuda, and H. Matsumura, *Appl. Phys. Lett.* **86**, 113115 (2005).

²²G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996); G. Kresse and D. Joubert, *ibid.* **59**, 1758 (1999).