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Polymer Electrolyte-Gated Carbon Nanotube Field-Effect Transistor

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ABSTRACT

Single-walled carbon nanotube field-effect transistors were fabricated using solid electrolyte (PEO plus $LiClO_4$) as gating materials. The SWNT FETs demonstrated strong gate-channel coupling with improved device characteristics compared with back-gated devices. More importantly, the nanotubes can be easily doped using different concentrations of electron acceptor mixed in the polymer materials. The transport type of the devices can be easily controlled through doping.

Discovered in the early 1990s,[1,2] single-walled carbon nanotubes(SWNTs) are attractive materials for many research fields. Using them in molecular-scale electronic devices is one of the most commonly proposed applications.[3] From both theoretical expectations[4] and experimental results,[5,6] SWNTs have been divided into two groups: metallic or semiconducting. Semiconducting SWNTs are of special interest because they are promising in producing semiconducting devices that rival devices made by traditional Si technology. In this report, we focus on the fabrication of field-effect transistors (FET), a core component for logic circuit fabrication,[7] with SWNTs.

In early work on nanotube FETs, a back-gating structure, which used the underlying highly doped Si substrate as the gate electrode, was often used because of its ease of fabrication,[8] but device performance was the trade off for such ease. To improve the FET performance, more complex structures and more expensive materials have been used in making nanotube FETs. For example, Appenzeller et al.[9] used HfO_2 as the insulating layer; Javey et al.[10] used ZrO_2, which has a very high dielectric constant, to constructed SWNT logic gates. They all succeeded in improving device performance greatly; however, the materials are expensive, and the fabrication processes are time-consuming. Meanwhile, the traditional FET structure of having a dielectric material between the gate and conducting channel was not abandoned in this work.

Here we introduce a new idea of using low-cost materials and easy processing procedures to fabricate nanotube FET devices with good device performance. This idea is motivated by the work done by Kruger et al.[11] and Rosenblatt et al.,[12] where salty water was used as a gate material and gate-channel coupling was enhanced by orders of magnitude. However, although the device performance is very good, the use of a liquid in devices presented practical problems in real electronic devices. Here, we demonstrate that the replacement of salty water with a polymeric solid electrolyte material can achieve similarly good device performance and avoid the problem of using a liquid in the devices. More importantly, the addition of different chemicals at controlled concentrations to the solid electrolytes enables us to control the device behavior. P-type, n-type, and ambipolar transistor devices can be controllably produced using the method.

Solid electrolytes (SEs), which are under intensive study as electrolytes in dry batteries, are formed by dissolving salts in polymers instead of water.[13] Their electric conductivity was first discovered by D. E. Fenton.[14] A representative material of this family is a lithium perchlorate/poly(ethylene oxide) (PEO) mixture, and its conducting mechanism involves the segmental motion-assisted diffusion of lithium ion in a PEO matrix. At the electrode−electrolyte interface, the ion flow was stopped before a chemical reaction could occur, hence a double layer of opposing charges is formed between the gate material and conducting channel material and is held as long as the gate voltage does not exceed the threshold for electrochemical reactions.

Additionally, for future nanotube-based electronics, the ability to "dope" the nanotubes selectively to achieve different device behavior is highly desired. SWNT FETs are mostly p-type FETs when fabricated under ambient condition,[10−12,15,16] but n-type FETs are also necessary when making complementary logic gate circuits, which have shown many advantages over logic circuits consisting of unipolar nanotube FETs.[17] Researchers from many groups have developed methods involving potassium doping in vacuum,[18] annealing in vacuum,[19] annealing in hydrogen,[10] and coating with polyethyleneimine (PEI)[15] to convert the as-made p-type SWNT FETs into n-type FETs. Here. We show that mixing different concentrations of 2,3-dichloro-5,6-dicyanobenzo-

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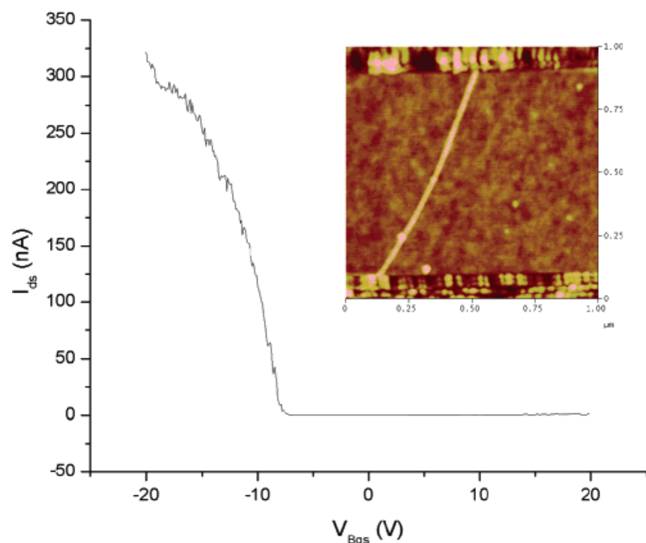

Figure 1. Transfer characteristic of a freshly made SWNT FET device. Gate voltage is applied via the SiO_2/Si back gate. Measurement was performed at V_{ds} = 20 mV. (Inset) AFM image of the same device; the diameter of the nanotube is around 2.4 nm.)

quinone (DDQ) into PEO could achieve both p-type and n-type FETs.

In our experiments, the nanotube devices were prepared using electron beam lithography (EBL) with poly(methyl methacrylate) (PMMA) as the resist. Briefly, the fabrication process started with the chemical vapor deposition (CVD) growth of SWNTs on SiO_2/Si wafers by using Fe/Mo nanoparticles as the catalyst[20]. Gold electrodes (30 nm thick) were then patterned to form devices using EBL without the use of any additional adhesion layer. Using gold electrodes without adhesion layers yields devices with consistently low contact resistances. The spacing between the source and drain electrodes, which varied between 1.5 and 1 μm, and the diameter of the SWNT bridging source and drain electrodes were both determined by atomic force microscopy (AFM). Device measurements were performed on a homemade probe station and the measurement setup consisting two Keithley 2400 source meters. Solid electrolytes were prepared by dissolving $LiClO_4$ and PEO (MW 100 000) in methanol to form a precursor. The precursor was then applied to SWNT FET devices followed by 90 °C baking to remove residual moisture and alcohol. The gate voltage was applied by piercing a third probe into the polymer layer after it dried. All chemicals were from Aldrich Chemical Co., Inc.

Figure 1 shows the AFM image and the $I_{ds}-V_{gate}$ curve of a representative device with a single nanotube between two metal electrodes; p-type behavior is routinely observed and is generally considered to be an effect of oxygen adsorption from air on SWNT side walls.[21] The conductivity of the device changes by a few orders of magnitude as a function of the gate voltage. (The gate voltage was applied using Si back gate.) After a layer of PEO + $LiClO_4$ mixture was applied to the top of the device, the device was converted into an n-type FET with the $I-$gate curve shown in Figure 2a. It was reported previously that the electron donor and acceptor could affect the carrier type in SWNTs.[21,22] An electron donor absorbed on the tubes would result in an n-type SWNT FET, while an electron acceptor would make it p-type. Therefore, our observation could be explained by

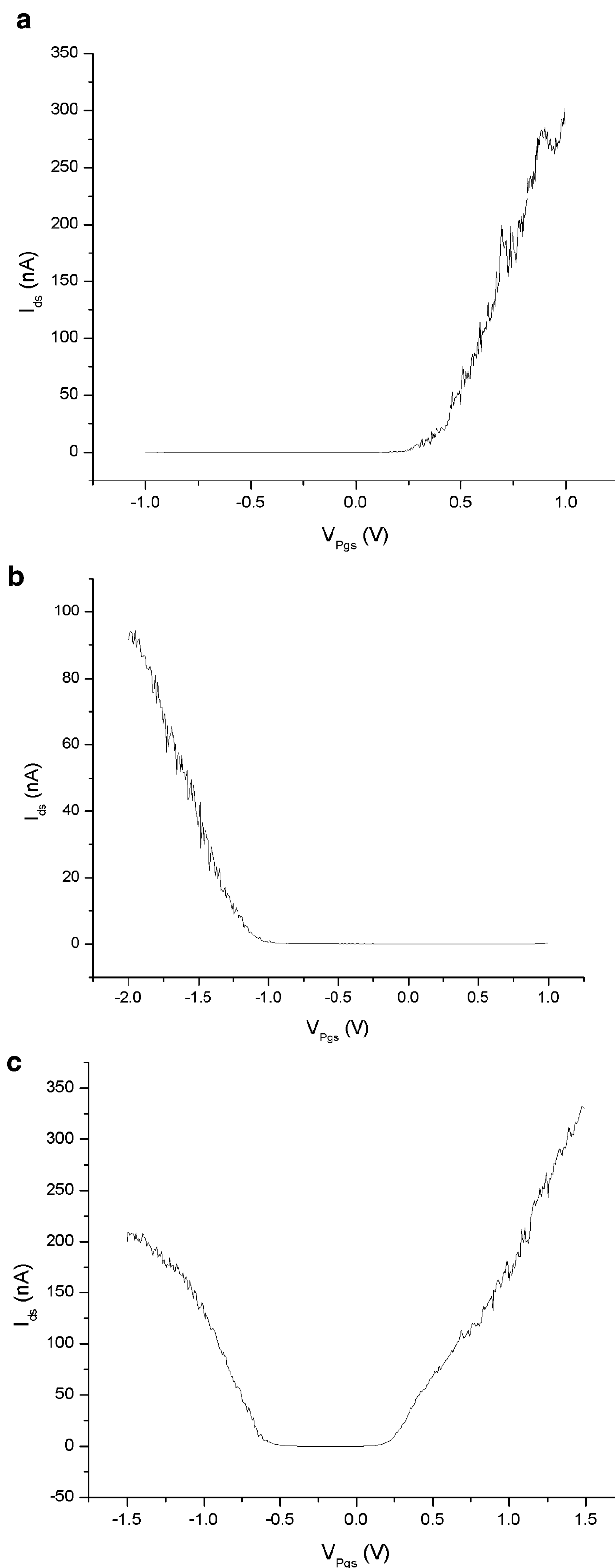

Figure 2. (a) n-type nanotube FET behavior after coating with PEO (PEO/$LiClO_4$(weight ratio) = 1:0.12). (b) p-type FET behavior with a high concentration of DDQ mixed into PEO (PEO/$LiClO_4$/DDQ(weight ratio) = 1:0.12:0.075). (c) Ambipolar FET behavior at low DDQ concentration in PEO (PEO/$LiClO_4$/DDQ(weight ratio) = 1:0.12:0.015). All measurement were performed at V = 20 mV.

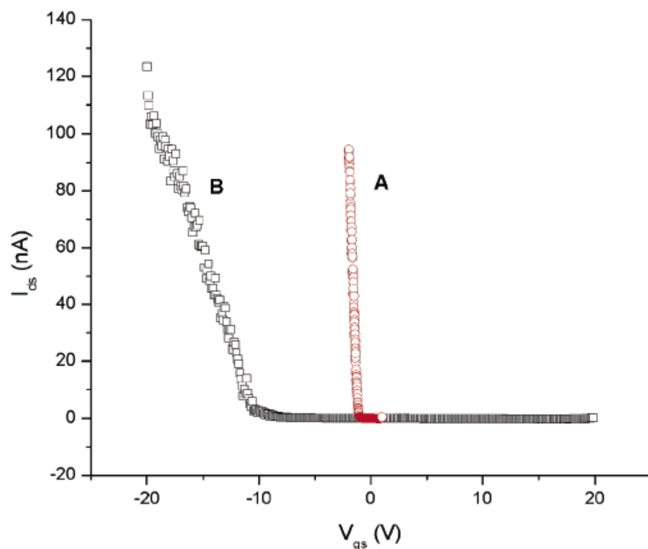

Figure 3. Comparison between back gating and top polymer gating on the same device. (A) Top polymer gating. (B) Back gating with a 1000-nm SiO_2 insulating layer. V_{ds} = 20 mV for both measurements.

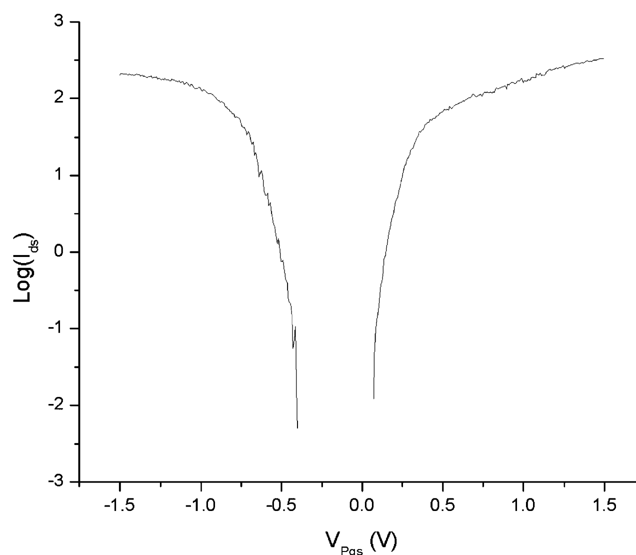

Figure 4. Typical curve of I_{ds} vs V_{gs} of an ambipolar device with the current plotted on a log scale. V_{ds} is 20 mV for the measurement.

the donation of an electron from the lone pair electrons on the oxygen atom in PEO toward the SWNT sidewall, which compensated for the p-type doping effect from oxygen molecules physically adsorbed on the tubes. It is also possible that oxygen molecules are dissolved in the PEO matrix and no longer contribute to the doping of the nanotube. Nevertheless, a conversion from p-type to n-type was always observed once the PEO + $LiClO_4$ mixture was applied onto an SWNT FET device. To maintain the p-type behavior of the original device, we added DDQ to the polymer precursor because DDQ is considered to be a strong electron acceptor. Interestingly, we have found that the concentration of DDQ in the polymer mixture had a strong effect on the device performance. At a high DDQ concentration (PEO/$LiClO_4$/DDQ(weight ratio) = 1:0.12:0.075), the devices were converted to p-type as we had expected (Figure 2b). At a low concentration (PEO/$LiClO_4$/DDQ(weight ratio) = 1:0.12:0.015), however, the device was converted to an ambipolar device (Figure 2c). A possible explanation for such an observation can be obtained by assuming that different doping levels allow different shifting of the Fermi levels: lower concentrations of DDQ cause the PEO doping effect to prevail, and the Fermi level of the tubes is close to the conduction band, whereas higher concentrations of DDQ would dominate the doping effect and would make the Fermi level of the tube shift to a location closer to valence band. However, it is also possible that the DDQ molecules altered the work functions of both the nanotube and the metal electrodes because the work functions of the metal electrodes play a very important role in the device behavior.[16,23,24] The exact origin of such a change in device performance is still under study in our group and would be of both practical and fundamental interest.

The use of a polymer electrolyte as the gate material improved the gate−channel coupling significantly. Figure 3 compares the difference in gating efficiency between back gating and top polymer gating. The effectiveness of how the gate voltage modulates the SWNT Fermi level is normally described by a device parameter called the subthreshold swing (S). It can be determined experimentally by using the following equation:

$$S = \frac{d(\log G)}{dV_g}$$

In the device shown in Figure 3, the S value reaches 100 mV/dec for polymer gating. Our devices normally gave S values ranging from 70 to 120 mV/dev for polymer gating. And the back-gating measurement normally gives an average S value of about 1 V/dec. According to MOSFET theory,

$$S = \left(\frac{kT}{e}\right) \ln 10\left(1 + \frac{C_D}{C_i}\right)$$

where k is the Boltzmann constant, T is the absolute temperature, e is electron or hole unit charge, C_D is the depletion-layer capacitance, and C_i is the gate capacitance. When C_D/C_i reaches zero, the gate coupling is considered to reach its limit, which is 60 mV/dec. We used the S value here because it is still a valid criterion for evaluating our gating effectiveness, although the theoretical limit of 60 mV/dec might fail when SWNT FETs do not follow such a traditional model.[25] In the previous SWNT FET device-making reports by Javey et al.[16] and Wind et al.[26] S values of 70 and 130 mV/dec were obtained, respectively. Therefore, the polymer-gated devices shown here not only are easy to fabricate but also provide good coupling between the gate and the nanotubes. In addition, the use of a polymer electrolyte as a gate material does not introduce a large leaking current at low bias voltage, as shown in Figure 4; the typical on/off ratio of the device currents is 3 to 4 orders of magnitude, which is actually limited by the instruments

used in our device measurements. We believe the real ratio could be higher.

We believe that the reason for the excellent gate coupling of the polymer-gated devices is the intrinsically large capacitance of the polymer electrolyte gating mechanism. Much like the salty water-gated nanotube devices reported previously,[12] the total gate capacitance, which determines the charging of the tube under a certain gate voltage, consists of electrostatic (C_e) and quantum (C_q) components. For back-gating device, C_{ebg} is given by

$$C_{ebg} = \frac{2\pi(\epsilon\epsilon_0)}{\ln\left(\frac{2h}{r}\right)}$$

in the "cylinder-above-plane" model,[27] where ($\epsilon\epsilon_0$) is the gate material dielectric constant, h is the gate thickness, and r is the nanotube diameter. The calculated capacitance per unit length of our 1000-nm SiO_2 back gating is 2.7×10^{-11} F/m. The total capacitance would be 2.5×10^{-11} F/m with a quantum capacitance of 4×10^{-10} F/m included[12]. The polymer electrolyte top-gating electrostatic capacitance C_e[27] is given by

$$C_e = \frac{2\pi\epsilon\epsilon_0}{\ln\left[\frac{r + \lambda_D}{r}\right]}$$

where $\epsilon\epsilon_0$ is the PEO dielectric constant, λ_D is the Debye screening length resulting from ion solvation, and r is the nanotube radius. Assigning a Debye length to be 1 nm[28], we get $C_{etg} = 2.6 \times 10^{-10}$ F/m. If the quantum capacitance of SWNT, about 4×10^{-10} F/m, is considered, then the total capacitance of the top-gated structure is about 1.6×10^{-10} F/m. Because the higher the capacitance, the better the gate−channel coupling and because our polymer-gated structure has an order of magnitude higher capacitance than that of the back-gated structure, much improved gate coupling is achieved. Although the Debye length varies with different salt concentrations, the estimated Debye length used in the calculation is still valid because the total capacitance variation caused by the change in the Debye length is small as long as it is still on the order of a few nanometers.

The device performance above the subthreshold region is normally evaluated by "transconductance". Figure 5. shows $I-V$ curve sets of a converted n-type device and a p-type device with DDQ doping. The transconductance reaches 5−6 μS, and the diameter-normalized transconductance is 2500−3000 S/m if an average diameter of 2 nm is taken. This value is also among the best parameters ever achieved in the SWNT FET field. However, there is still room for improved SWNT FET transconductance because it is limited primarily by the nonideal contact between the tube and electrode. If we could obtain true ohmic contact between nanotubes and SWNTs, which has recently been realized,[16] then the transconductance at moderate drain bias should reach a higher value. Additionally, the $I-V$ behavior of the p-type

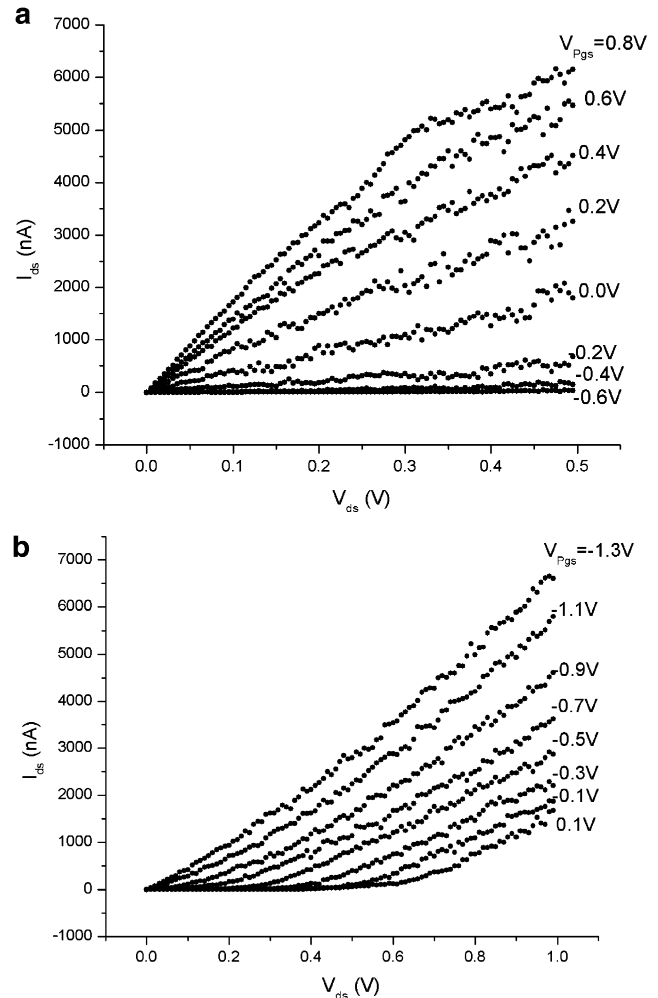

Figure 5. (a) Output curve of an n-type SWNT FET device made with top polymer gating, (b) Output curve of a p-type SWNT FET device made with top polymer gating.

devices is different from that of previously observed p-type devices without a polymer coating. The curve shape cannot be fit to a standard square-law model for a diffusive channel.[7] We believe that this may be caused by the nonohmic contact between the electrodes and the doped nanotubes. More detailed study is underway to gain a better understanding of the origin of such phenomena.

In conclusion, we used a new approach to fabricate SWNT FET with solid electrolyte as the gate material. The resulting devices have excellent device performance compared with that of the back-gated nanotube FETs. The main reason for such good performance is due to the interface double-layer formation between the gate materials and conducting channel, which enhanced the gate−channel coupling by an order of magnitude. At the same time, this new approach offers the advantage of an easier fabrication process to make complicated logic circuit devices because the polymer electrolyte is easier to pattern on the surface using photolithography as well as soft lithography.[29] Finally, the use of polymer electrolytes as gating materials makes it convenient to control the device behavior of the produced devices. n-type, p-type, and ambipolar transport in the FET channel can be controlled by varying the concentration of small organic molecules such

as DDQ in the polymer matrix. However, the response of the polymer-gated devices under high-frequency ac signals is still under investigation. It is possible that the diffusion of ions needed for the formation of double layers will limit its application at high frequency. Nevertheless, the outstanding dc performance and the easy control of the device types, which cannot be achieved by conventional Si technology, would make nanotube-based electronic devices more attractive for future applications.

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