Transformation of Unipolar Single-Walled Carbon Nanotube Field Effect Transistors to Ambipolar Induced by Polystyrene Nanosphere Assembly

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ABSTRACT We have fabricated single-walled carbon nanotube (SWNT) field effect transistors (FETs) with molybdenum source and drain contacts. Normally, these devices operate only as p-channel transistors, however, after polystyrene latex nanospheres were attached to the nanotubes close to the contacts, they changed to ambipolar operation. This strategy provides a simple method to modify the electrical behavior of unipolar SWNT-FETs by influencing the gate-channel electric field distribution and offset charge, so enabling complementary circuits to be fabricated.

KEYWORDS: Single walled carbon nanotube (SWNT) · field effect transistors (FETs) · ambipolar · polystyrene nanospheres

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Single walled carbon nanotubes (SWNTs) have been investigated as the active material for building electronic circuits, such as carbon nanotube field effect transistors (SWNT-FETs) and diodes.[1] Under ambient conditions, semiconducting SWNTs generally show unipolar p-type behavior and this has been attributed to the properties of the nanotube−contact metal junction.[2] It has previously been shown that oxygen, adsorbed at the metal−nanotube contact, pins the Fermi level near to the top of the valence band in the carbon nanotube, leading to exclusively p-type behavior.[3] N-type behavior can be induced by annealing in vaccum, but this approach is of limited applicability as the effect is reversed upon subsequent oxygen exposure. Unipolar SWNT-FETs can also be transformed into ambipolar transistors either by annealing in vacuum/inert atmosphere [2−4] or by gate structure engineering.[5,6] It has also been found that by using Ti for the metal contact, covered with a protective layer (*e.g.*, SiO_2 film) and then annealed in vacuum or in an inert atmosphere, the initial p-type transistor behavior could be gradually transformed into ambipolar behavior.[2] This change results from the formation of low resistance titanium carbide−carbon nanotube contacts for both electron and hole transport.[2,4] Polystyrene (PS) latex nanospheres have been widely used for self-assembly on hydrophobic surfaces, such as unoxidized silicon or gold.[7,8] In this paper, we report on the transformation of conventional unipolar SWNT-FET transistors into ambipolar devices by the assembly of PS latex nanospheres onto sections of the nanotube close to the metal contacts. It is a novel way of gate engineering.

RESULTS AND DISCUSSION

Charge transport in most CNT-FETs is strongly influenced by the nature of the Schottky barrier between the nanotube and the contact metal.[9] This Schottky barrier is due to the energy band misalignment at the nanotube/metal interface, which is determined by intrinsic material properties. There are two possible Schottky barriers in a SWNT-FET, one for the electrons and one for the holes. As long as one of the barriers is much higher than the other, the FET operates as a unipolar device and usually hole transport dominates in this type of device.[10] Here we present a simple process to change the device from unipolar to ambipolar behavior, using a layer of PS nanospheres. To investigate the mechanism for this effect, the behavior of devices with and without PS latex nanospheres were compared. SEM images of some of these devices

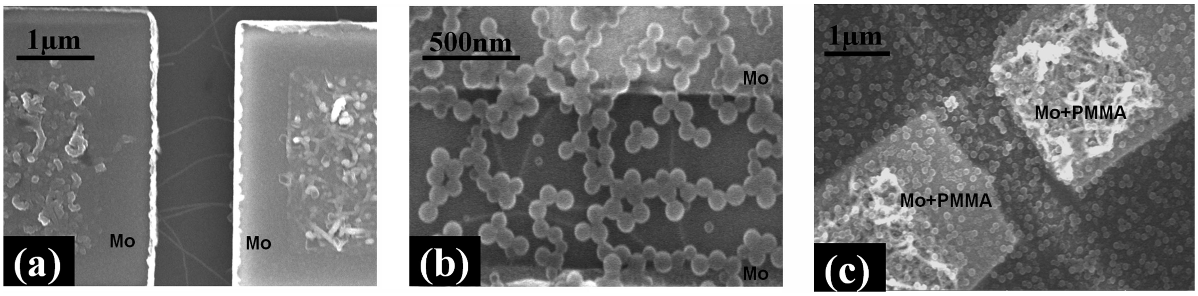

Figure 1. SEM images of (a) SWNT-FET, (b) SWNT-FET/PS, and (c) SWNT-FET/PMMA/PS.

are shown in Figure 1. The figure panels show (a) a conventional SWNT-FET, (b) a transistor with PS latex nanospheres assembled over the whole of the device (SWNT-FET/PS), and (c) a transistor similar to the previous case except that a patterned poly(methyl methacrylate) (PMMA) layer has been used to prevent the PS latex nanospheres from attaching to the sections of the nanotubes close to the metal contacts (SWNT-FET/PMMA/PS). As Figure 1a shows, the spacing between the metal contacts is around 1 μm, but the transistor channel length is dependent on the number and arrangement of semiconducting CNTs in each device. The assembled PS latex nanospheres in Figure 1b closely cover the Mo electrodes and the edges of the CNTs. The PMMA layer in Figure 1c has a window of 0.5 μm width defined by e-beam lithography close to the middle of the channel to limit contact between the PS latex nanospheres and the CNTs to just this region. These configurations are illustrated schematically in Figure 2. Figure 2a shows a device where the PS nanospheres have been allowed to assemble on any part of the nanotube or contact (as in Figure 1b), and Figure 2b shows a device where the PS nanospheres have been prevented from assembling onto the nanotube or contact except in a region ~0.5 μm wide at the center of the channel (as in Figure 1c). In addition, devices (SWNT-FET/PMMA) with an unpatterned PMMA layer were also tested for comparison.

Electrical characteristics of these devices were investigated by in-air probing at room temperature using programmable source-measure units. Measurements on unmodified SWNT-FETs indicate the usual p-type response with ON current $I_{ON} = 2.8 \times 10^{-6}$ A and an OFF current $I_{OFF} = 2.9 \times 10^{-11}$ A (at V_{DS} of 3 V), giving the device an on−off ratio of ~10^5. The subthreshold slope from a typical FET is ~1.1 V/dec (result shown in Figure 3a). The flat band voltage is around 0 V (or positive gate voltage), and saturation for hole transport does not occur until the gate voltage reaches about −20 V. The accessible positive gate voltage range was insufficient to induce electron conduction. However, after modification by a layer of PS latex nanospheres, the subthreshold slope for hole transport was greatly improved and the flat band voltage moved to around −10 V. The SWNT-FET/PS also showed an ambipolar response with a p-channel ON current of $I_{ON} = 6.3 \times 10^{-6}$ A, an n-channel ON current of $I_{ON} = 1.4 \times 10^{-8}$ A, and a slightly lower OFF current of $I_{OFF} = 6.4 \times 10^{-12}$ A. The on−off ratios for the SWNT-FET/PS are ~10^6 and ~10^3 and the subthreshold slopes are ~0.37 and ~1.02 V/dec for p- and n-channel of operation, respectively, as shown in Figure 3b.

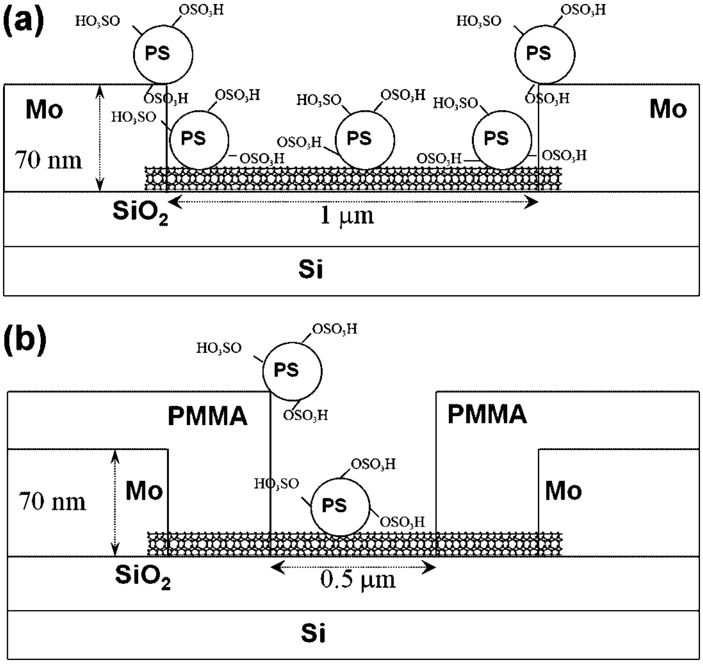

Figure 2. Schematic cross section of device SWNT-FET/PS (a), devices covered by PMMA with a window of 0.5 μm width after coating with PS nanospheres (SWNT-FET/PMMA/PS) (b); not to scale.

One possible cause for the change in device behavior is the presence of excess charge on the PS latex nanospheres either from the residual colloidal stabilization charge, whose contribution is expected to be weak, or from the electric field induced charge storage in the PS nanospheres. Excess charge stored on the nanosphere will cause the shift in the threshold voltage seen in Figure 3b com-

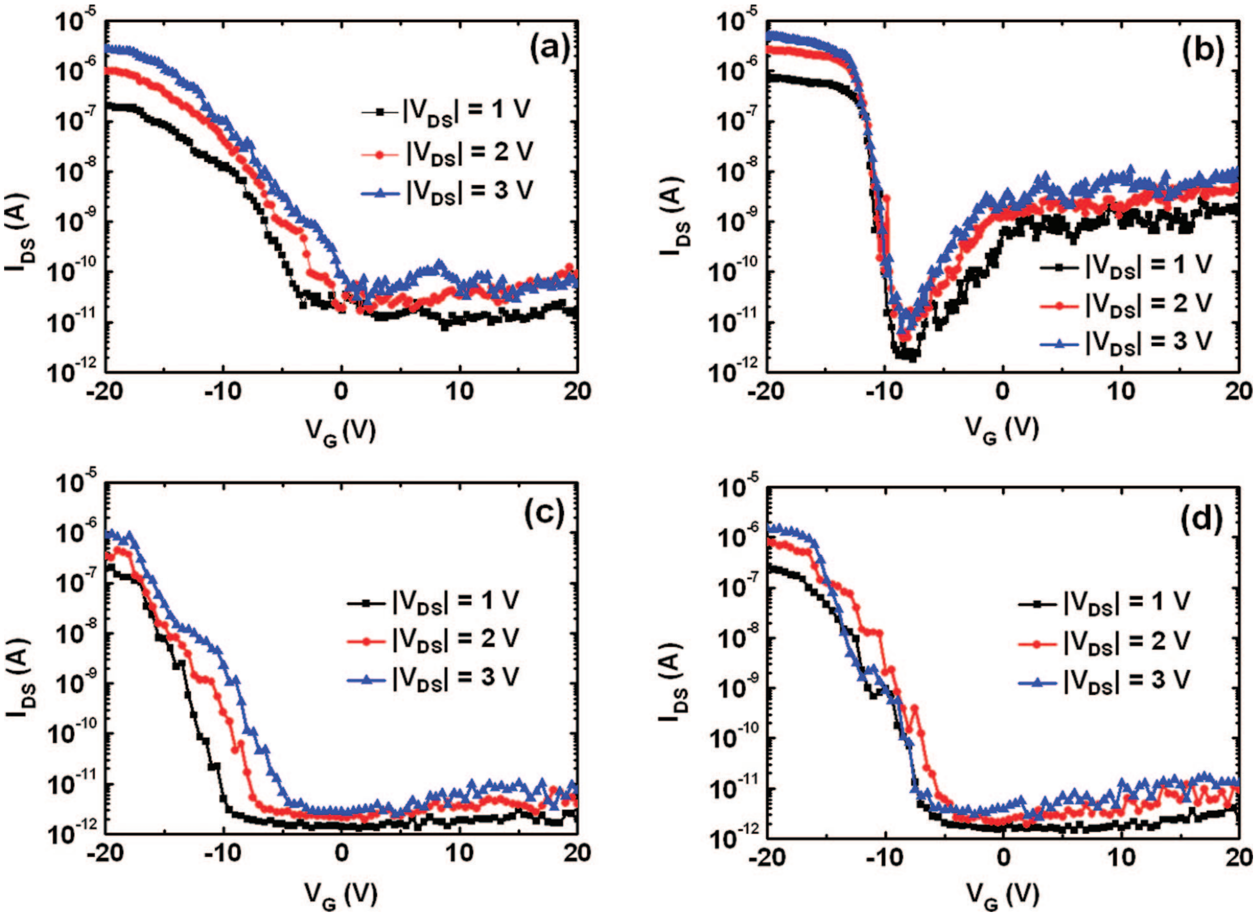

Figure 3. Drain current *vs* gate voltage characteristics measured in air and at room temperature for drain voltage 1 (), 2 (●) and 3 V (▲): (a) SWNT-FET, (b) SWNT-FET/PS, (c) SWNT-FET/PMMA, and (d) SWNT-FET/PMMA/PS.

pared to Figure 3a. However, any excess charge can only explain the shift in the flat band voltage, but cannot cause a change in the subthreshold slope.

The work function of the contact metal is known to influence the current–voltage characteristics of the SWNT-FETs.[11,12] The presence of an interfacial layer at the metal–nanotube contact could modify the effective work function and so influence the device behavior. However, chemical reactions between the surface coating on the PS latex nanospheres or the counterion solution and the contact metal is not possible due to the chemical stability of the contact metal and due to the nanotubes being grown directly from a catalyst, that is subsequently encapsulated by the contact metal before the nanosphere assembly takes place. It is also unlikely that ions in the nanosphere solution resulted in n-type doping due to the nature of the solution. In addition, such a mechanism would have worked even in the case of coverage of the contact areas with PMMA (which is porous to many ions).

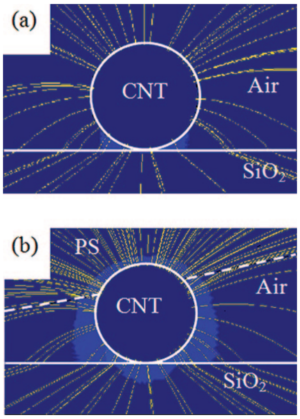

Figure 4. 2D simulation of the electric field distribution around (a) a CNT and (b) a CNT next to a PS nanosphere. In each case, the diameter of the CNT is 1 nm and it is resting directly on a silicon dioxide gate dielectric of thickness 100 nm. The diameter of the PS nanosphere is 100 nm and only parts of the gate dielectric and of the PS can be seen due to the scale. The spatial distribution of the electric field is indicated by the streamlines and the field strength is indicated by the background color.

The influence of the gate on the current–voltage characteristics of SWNT-FETs have been discussed in refs 9, 10, and 13. The profile of the energy bands, characterizing the Schottky barrier of the SWNT-FET, is influenced by the gate voltage (V_G), the drain bias (V_{DS}), and the gate capacitance of the FET. Quantum mechanical effects have an important consequence on how V_G affects this energy barrier.[9] Typically, carrier transport through the metal–CNT contact is dominated by quantum mechanical tunnelling through the barrier rather than thermally activated emission over the barrier,[10,13] so that the thickness of the Schottky barrier is critical in determining device behavior. An increase in gate capacitance would have the effect of reducing this barrier at the same V_G and V_{DS}. The mechanism for this increase can be understood from the effect of the PS latex nanospheres on the electric field distribution between the gate electrode and the nanotube, as shown in Figure 4. The relative permittivity of the latex is significantly higher than that of air, so that an increase in gate capacitance is expected from the displacement of air when the PS latex nanospheres are attached. However, covering the whole nanotube with PMMA (which has a similar relative permittivity to that for latex) did not result in ambipolar behavior. Because of the great difference in size between the nanotube (diameter ≈ 1 nm) and the nanosphere (diameter ≈ 100 nm), the shape of the nanospheres also influences the change in gate capacitance. There are two factors mainly influencing the ambipolar behavior, the permittivity and the geometry of materials surrounding the nanotube. Encapsulating the nanotube with PMMA results in a very small enhancement of the local electric field. However, the shift in the threshold voltage is still present in Figure 3c and 3d compared to the conventional device due to charge storage at the oxide−PMMA interface. Finite element modeling by COMSOL has been used to investigate the effect of a PS nanosphere on the electric field distribution around a CNT. Figure 4 shows the results from a 2D simulation of the electric field distribution close to the CNT for a device without (a) and with (b) a PS nanosphere. In both cases the CNT is at ground potential and the electric field is due to a gate voltage (from an electrode below, outside of the diagram). In the case of the CNT alone, the electric field is strongest on the side closest to the silicon dioxide. In the case of the CNT with the PS nanosphere, there is a significant increase in the electric field around the CNT in the region where the PS makes contact. The relatively low stiffness of the PS greatly increases this contact area compared to the SiO_2/CNT contact area. This results in an increase in the total electric flux terminating at the CNT in the case of the CNT with a PS nanosphere compared to the case of the CNT alone. A 2D simulation underestimates this increase in the electric flux as field lines are concentrated from a wide area covered by the PS nanosphere to a small area defined by the CNT/PS contact. 3D modeling (not shown) suggests that an overall field enhancement of 1 order of magnitude is possible.

The electric field increase due to the presence of the PS nanosphere occurs locally to the point of contact between the CNT and the PS. Since this area of contact is very small and since there is a relatively small number of contacts along the CNT, the total electric flux seen by the CNT is not greatly increased. However, if the CNT is defective (as expected for carbon nanotubes grown by this method), it will behave electrically as a number of short lengths separated by tunnel barriers (formed by the defects). The increase in electric flux due to the contact with a PS nanosphere is then effectively confined to a length of the CNT between tunnel barriers. As discussed earlier, the unipolar nature of this type of CNT-FET is due to the nature of the barrier at the metal−CNT contact. If the band offset is large, then one carrier type experiences a significantly larger barrier than the other type, giving rise to the observed unipolar transport. An increase in the gate coupling to the CNT can be used to overcome this effect, but may require an unacceptably small gate dielectric thickness. Since the barrier occurs close to the CNT-metal contact, a local increase in the gate coupling can achieve the same result for defective carbon nanotubes. This explains the observation that ambipolar behavior is only seen when the PS nanospheres are able to contact the nanotube in the regions close to the metal−CNT contact. The increase in gate capacitance is also effective in improving the subthreshold slope, as well as the ON and OFF currents, as seen in Figure 3b.

CONCLUSION

In summary, this paper discusses an alternative strategy to make ambipolar SWNT-FETs by modifying conventional nanotube transistors using PS latex nanospheres. Nanospheres modify the gate electric field distribution around the CNT through the local concentration of electric field lines at the point of contact between the CNT and the nanosphere. This increases the gate capacitance and if this occurs close to the metal-CNT contact, then greater control over the Schottky barrier is realized. This simple method enables ambipolar transistor operation and a great improvement in the subthreshold characteristics and may have applications to complementary logic circuits, memory devices, and biosensor arrays.

EXPERIMENTAL DETAILS

SWNT-FET devices were fabricated on an n-type Si substrate with a 1 μm thick layer of thermally grown SiO_2 as the insulating dielectric, so that the substrate could be used as a bottom-gate electrode. SWNTs were deposited by chemical vapor deposition using acetylene (C_2H_2) gas at ~900 °C for 15s on a patterned triple-layer metal film (10 nm Al/1 nm Fe/0.2 nm molybdenum (Mo)), with Fe as the active catalyst for CNT growth. Source and drain contact electrodes were patterned by electron beam lithography, Mo sputtering (~70 nm thickness), and lift-off. Each FET contains a random mixture of metallic and semiconducting SWNTs in the channel. The metallic nanotubes were selectively removed from the channel conducting pathway by using current-induced breakdown, leaving intact only the semiconducting nanotubes.

PS latex particles (Aldrich) with an average diameter of 100 nm (1 wt % dispersion in water) were drop cast onto SWNT-FETs previously showing unipolar operation. The aqueous layer was allowed to evaporate naturally so that the PS nanospheres assembled by a capillary process on the Mo electrodes and inside the channel. These PS latex nanospheres were surface-terminated with sulfate groups to make them soluble and suspendable in aqueous solution. This surface termination can give rise to an excess charge, which contributes to the stability of the colloid when in solution. As the water evaporates, the counterions in the aqueous solution are attracted to the surface of the nanospheres, where they neutralize the excess charge. If this process is not complete before all the water has evaporated then some excess charge will remain on the surface of the nanospheres.

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