Short-channel effects in contact-passivated nanotube chemical sensors

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We report a design for carbon nanotube field-effect transistors which tests the nanotube depletion length. In this design, the metal contacts and adjacent nanotubes were coated with impermeable silicon oxide, while the central region of nanotubes was exposed. We tested the devices by measuring sensitivity to NH_3 and poly(ethylene imine). NH_3 caused similar responses in passivated devices and in normal, nonpassivated devices. Thus, the device design passivates the metal-nanotube contacts while preserving chemical sensor characteristics. Poly(ethylene imine) produced negative threshold shifts of tens of volts, despite being in contact with only the center region of devices. Based on the observed device characteristics, we conclude that the length scale of the covered nanotubes in our structure is comparable to the decay length of the depletion charge in nanotube transistors. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1619222]

Field-effect transistors (FETs) using semiconducting single-walled carbon nanotubes (NTs) as active elements[1–3] have been extensively studied. Because of their unique nature as one-dimensional conductors with extremely high surface areas, nanotube devices have been found to be sensitive to gases[3–5] and biomolecules,[6] leading to the notion that these devices can serve as chemical or biological sensors. There is still little understanding of the remarkable sensitivity of nanotube devices to their chemical environment, such as threshold voltage changes of several volts in the presence of only 0.1% NH_3 in air.[4] Sensing may occur through charge–transfer doping of the nanotube channel of the FETs.[7,8] Alternatively, the sensing could be dominated by the interaction of molecules with the metal contacts or the contact interfaces. Adsorbed molecules would modify the metal work functions, modifying the Schottky barrier.[9,10] Heinze *et al.*[7] have assigned the effect of oxygen to the Schottky barrier and the effect of potassium to nanotube doping.

For the device architecture traditionally employed, both mechanisms are operable. A simple, clear test of the models discussed above would be desirable. Previous chemical sensing experiments have been performed with devices in which both nanotubes and the nanotube-metal contacts were directly exposed to the environment. Devices have also been studied with permeable layers applied to the contacts, such as poly(methyl methacrylate) (PMMA).[10–12] We have fabricated a device architecture, in which the interface between the metallic contacts and the nanotubes is covered by a passivation layer, referred to as contact-passivated (CP). In such a configuration, with the junction isolated and only the central length of the nanotube channels exposed, the contacts should not respond to chemicals. At the same time, the section of the device which is open to the environment can be doped via charge transfer.

Single-walled carbon nanotube (SWNT) FETs were fabricated using nanotubes grown by chemical vapor deposition.[13,14] Electrical leads (35 nm Ti, 5 nm Au) were patterned with a gap of 0.75 μm between source and drain. Three types of devices were prepared. Nonpassivated (NP) devices received no passivation layer. Fully passivated (FP) devices were completely covered with a 70 nm silicon monoxide layer. The experimental configuration, referred to as contact-passivated (CP), included a liftoff-patterned SiO layer deposited by thermal evaporation. The layer extended over the leads and for several hundred nanometers on either side, as depicted in Fig. 1. This geometry was chosen to protect a length of nanotube significantly longer than a few nanometers, the estimated length of the metal-nanotube Schottky barrier.[15]

Devices were tested for their sensitivity to NH_3 and poly(ethylene imine) (PEI). NH_3 testing was performed in air using a gas nozzle. For PEI testing, devices were coated with PEI,[16] and their electrical characteristics were compared be-

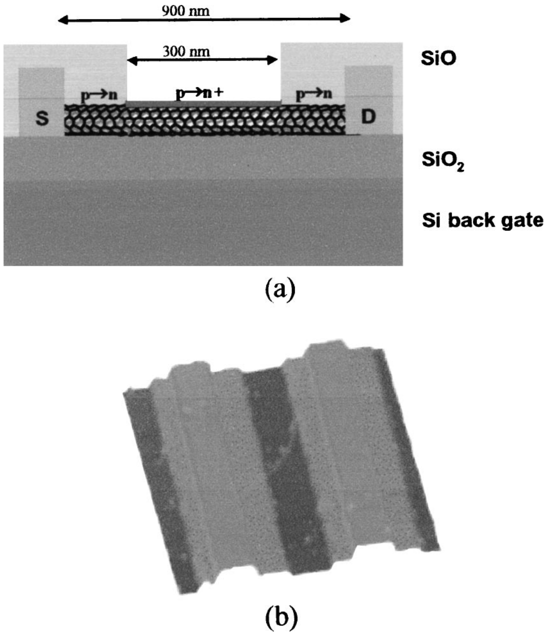

FIG. 1. (a) Device design, including the SiO passivation over the Ti/Au electrodes and neighboring area. The center of the device, which is left bare of SiO, is exposed to NH_3 or PEI. (b) Atomic force microscopy image of the SWNT contact passivated device after deposition of PEI. The image size is 2.75 μm.

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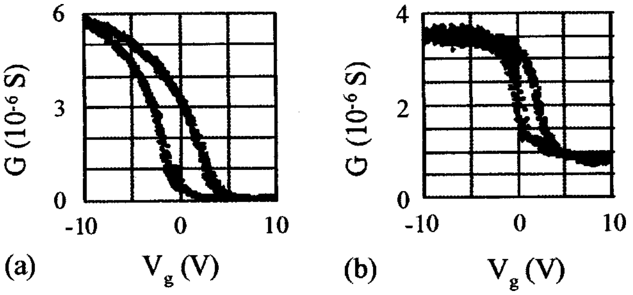

FIG. 2. Electrical properties of the SWNT devices at room temperature before and after passivation. Conductance vs gate-voltage $G-V_g$ curve (100 mV bias). (a) non-passivated NT device and (b) SiO contact-passivated NT device.

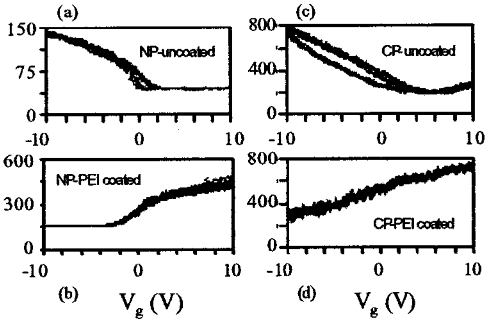

FIG. 4. The effect of PEI coating on transfer characteristics. (a) Nonpassivated NT device before coating; (b) nonpassivated NT device after coating; (c) contact-passivated NT device before coating; and (d) contact-passivated device after coating.

fore and after coating. Passivated substrates were soaked overnight in a solution of PEI (average molecular weight ~25 000, Aldrich) at 20% by weight in methanol and then rinsed with methanol. By atomic force microscopy, a thin layer (~3 nm) of PEI was observed to coat the devices. Electrical measurements were performed in vacuum to minimize hysteresis with respect to the gate voltage.[14,17]

Measurements of source-drain current versus bias voltage were linear. As the transfer characteristic shown in Fig. 2(a) indicates, the devices were *p*-type FETs, containing several nanotubes with occasionally a metallic nanotube included. The transfer characteristic, i.e., the conductance versus gate voltage, of a representative CP device is shown in Fig. 2(b); these devices operate as transistors similar to NP devices.

Figures 3(a), 3(b), and 3(c) compare the effects of pure NH_3 exposure on NP, FP, and CP devices. The substrates were repeatedly exposed to gas briefly and allowed to recover in air. For the NH_3 exposure, the gate voltage was maintained at -10 V. In these circumstances, NP devices exhibited large decreases in conductance during exposure to NH_3,[4] and they recovered to one-half their original conductance levels after the removal of the gas. FP devices exhibited very small changes, and they did not recover after exposure. CP devices exhibited changes nearly as large as the changes in NP devices, and the changes were more reversible.

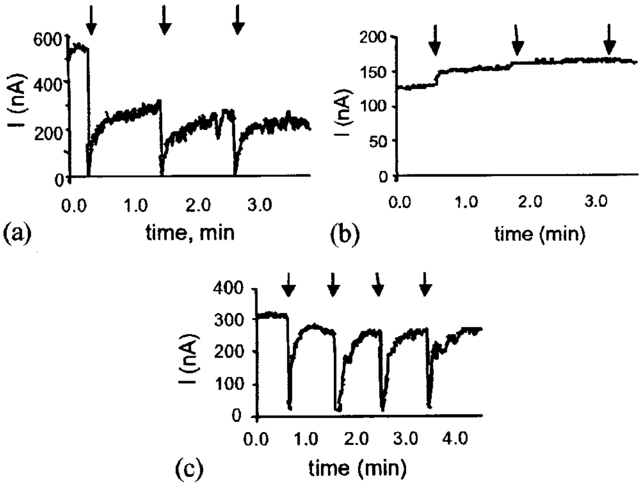

FIG. 3. Electrical response of SWNT device to gas. Current vs time (100 mV bias) recorded with short exposures to NH_3 with arrows indicating exposures. (a) Nonpassivated NT device with NH_3; (b) SiO fully passivated; (c) SiO contact-passivated. The metallic nanotube current has been subtracted from all three curves.

Next, we will describe the effects of PEI. FP devices were not affected by PEI coating. In both NP and CP devices, the results of PEI coating varied between devices. Inspection by atomic force microscopy suggested that the variation was due to the occasional deposition of polymer coils on the nanotubes. In addition, all devices were observed to have much wider hysteresis loops after coating when measured in air. We attribute the hysteresis to the moisture content of the PEI coatings.[17] Because the hysteresis obscured the device characteristics, samples were exposed to vacuum to observe the native device behaviors. The width of the hysteresis loops decreased during vacuum drying. After several hours in vacuum, devices exhibited significantly decreased hysteresis; the device characteristics measured after drying are shown in Fig. 4.

Despite the variations, several general observations can be made, illustrated by the device characteristics in Fig. 4. The minimum and maximum conductances observed in a device generally did not change by more than 10%. All devices exhibited a shift in their transfer characteristics. The *p*-type threshold voltages shifted towards more negative gate voltages, frequently so far as to be unobservable with our range of gate voltages. Similarly, the *n*-type threshold voltages, which were visible for some unmodified devices, shifted left. For the CP device shown, no clear *n*-type threshold was observed even at -10 V.

These results have specific implications for the models of nanotube chemical sensing. Mechanisms can be distinguished[7] by their focus on nanotube channel doping or on metal work function variation. We will first discuss the sensitivity of contact-passivated devices to NH_3. The observation that these devices are almost as sensitive as nonpassivated devices indicates that the contacts can account for at most a few percent of the sensitivity. The lack of gas sensitivity in FP devices demonstrates that the metal-nanotube contacts are protected from gas exposure by the passivation layer. The large response in CP devices is therefore not the result of changes at the contacts. Heinze *et al.*[7] have previously concluded that NH_3 dopes nanotubes, based on models of the changes in the transfer characteristic. Our result is a further direct demonstration that NH_3 affects the channel rather than the contacts.

Similarly, the results of PEI coating are not caused by contact effects. The similarity between CP and NP devices that have been coated with PEI indicates that the channel plays the central role in the response to PEI. Indeed, the devices are more similar than might be expected, given that in CP devices fully one-third of the nanotube length is protected from the dopant. In comparison, Kong *et al.*[11] found that a PMMA-passivated device hardly conducted after doping. Thus, while the behavior of our devices shows the importance of the channel, it requires further explanation.

A key difference between the devices fabricated by Kong *et al.* and the devices reported here is the length of the nanotubes, which are relatively short in the present work. Therefore, we will discuss our devices in terms of long-channel and short-channel descriptions. In the long-channel case, the nanotube can be modeled as containing several regions, demarcated in Fig. 1(a), including the metal contacts, the two lengths of passivated nanotube, and the central length of exposed nanotube. However, as we will discuss, in our devices this model is not appropriate, because the channel is short enough to be comparable to the depletion length. The shortness of the channel accounts for the surprisingly strong doping effect of PEI in CP devices.

The failure of the long-channel description will be detailed first. Before coating, the entire nanotube is hole-doped.[5,18] After coating, the sections of nanotube under the passivation should remain unchanged except within a short depletion length. The central section, coated with PEI, is doped n type. The resulting device, consisting of metal–p–n–p–metal junctions, should operate as an enhancement-mode transistor. Conduction would only be possible under high gate voltage conditions that invert the n-type or p-type regions. By contrast, at zero gate voltage the PEI-coated CP devices conducted well. At the same time, threshold voltages in these devices shifted as far as -10 V. The transfer characteristics resemble those of n-type depletion-mode FETs, rather than the p–n–p enhancement-mode FETs predicted by a long-channel model.

Given that the long-channel description is not sufficient, a short-channel description must be considered, and the depletion length estimated. The depletion length in nanotube–nanotube heterojunctions was calculated by Léonard and Tersoff[19] to decay logarithmically with distance. Thus, the relevant length scale is the distance at which the charge density due to depletion decays to the dopant density. In the central, PEI-coated region, the dopant charge density can be estimated by supposing that each nanotube is covered with a monolayer of PEI. With one NH_2 group per 10 Å^2, this corresponds to one NH_2 group per six carbon atoms. If the donated charge is 0.02 electrons[20] per NH_2, this amounts to a dopant concentration of 10^{-3} carriers/carbon. By contrast, the density of p-type dopants (primarily oxygen)[3] in the passivated regions is much lower. It can be estimated using the calculations of Jhi *et al.*[18] for oxygen adsorption. According to their calculation, the binding energy of oxygen is 0.25 eV, and each oxygen molecule contributes 0.1 holes. Using the van't Hoff law to estimate the adsorption, the dopant concentration is approximately 6×10^{-5} carriers/carbon. This charge density is much lower than the density of charge induced at the junction with the n-type central region. According to the calculations in Ref. 20, the charge induced by 10^{-3} carriers/carbon will decay to 6×10^{-5} carriers/carbon at a distance of 800 nm from the junction. By comparison, the p-type passivated regions in our devices are only 300 nm long. Consequently, the depletion charge is comparable to the background charge throughout the passivated regions. Thus, although they are not directly doped by the PEI coating, the passivated regions are indirectly affected. To retain p-type channels would require significantly longer passivated regions. Thus, the strong similarity between CP and NP devices coated by PEI indicates that short-channel effects are important in these devices.

In conclusion, we have fabricated a NT–FET device architecture that features long passivated regions in a short device. We have used electrical measurements and response to chemicals to explore this architecture. The CP devices must be thought of not as three differently doped regions (p–n–p), but as one channel with a weakly varying Fermi level. They represent the first explicit realization of a short-channel nanotube device, in which the channel length is comparable to the length scale of charge depletion. The long range of depletion must be considered in the design and analysis of devices. In particular, it may help to explain chemical sensitivity, since local chemical doping can affect large regions of a device.

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