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COMMUNICATIONS

Published on Web 09/01/2004

Miniature Organic Transistors with Carbon Nanotubes as Quasi-One-Dimensional Electrodes

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Small organic molecules and conjugated polymers can be easily processed to afford functional electronics such as field effect transistors (FETs),[1a] and in principle, scaling[1b] to single-molecule-long devices could circumvent the low carrier mobility problem for these materials to afford high performance ballistic FETs.[2,3] For highly scaled molecular transistors with short channels, however, it is crucial to develop novel device geometries to optimize gate electrostatics needed for efficient ON/OFF switching.[4,5]

It is shown here that single-walled carbon nanotubes (SWNT) can be used as quasi-one-dimensional (1D) electrodes to construct organic FETs with molecular-scale width (~2 nm) and channel length (down to 1−3 nm). The favorable gate electrostatics associated with the sharp 1D electrode geometry allows for room temperature conductance modulation by orders of magnitude for organic transistors that are only several molecules in length, with switching characteristics superior to devices with lithographically patterned metal electrodes. We suggest that carbon nanotubes may prove to be novel electrodes for a variety of molecular devices.

We first developed a reproducible method of cutting metallic SWNTs to form small gaps within the tubes and with control over the gap size down to $L \approx 2$ nm. The cutting relied on electrical breakdown[6] of individual SWNTs between two metal electrodes (Figure 1a), and the size of the cut was found to be controllable by varying the lengths of the SWNTs (see ref 6b and Supporting Information). Organic materials were then deposited to bridge the gap in the vapor (for pentacene) or solution phase (for regioregular poly-(3-hexylthiophene), P3HT), forming the smallest organic FETs with effective channel length down to $L \approx 1-3$ nm and width ~2 nm.

With a cut metallic SWNT (gap $L \approx 5-6$ nm) bridged by a pentacene nanocrystallite (Figure 1b,c), we observed clear semiconducting FET characteristics in the current vs gate ($I_{ds} - V_{gs}$) curve (Figure 2a). The device exhibited a current modulation of $I_{max}/I_{min} \approx 10^5$ under gating at a fixed bias voltage of $V_{ds} = -0.5$ V. The drastic switching clearly differed from the original metallic SWNT device (lack of gate dependence, Figure 2a inset). This corresponds to the formation of a pentacene FET with channel length $L \approx 5-6$ nm and width of $w \approx 2$ nm (i.e., the diameter of the SWNT), as charge transport via hopping between pentacene molecules should be mainly confined in a width on the order of the tube diameter. Notably, the subthreshold swing of the device is $S \approx 400$ mV/decade (Figure 2a).

We varied the channel lengths L of SWNT-contacted pentacene FETs ($L \approx 1-3$ nm, $L \approx 5-6$ nm, and $L \approx 10-15$ nm, respectively) and observed length-dependent transport properties at various temperatures. At $T = 300$ K, the devices exhibited on-current I_{max} scaling approximately with $\sim 1/L$ (under $V_{ds} = -1$ V). This suggests that the active channel lengths for the SWNT-contacted pentacene FETs are set by the gap sizes in the cut tubes and that the channel resistance appears to be a dominant part of the resistance of the devices. At $T \leq 4$ K, only the shortest pentacene FETs with $L \approx 1-3$ nm consistently (>5 devices) exhibited appreciable conductance (Figure 2d), while the longer ($L \approx 5-6$ nm and $L > 10$ nm) devices became insulating in the entire gate-voltage range. The $L \approx 1-3$ nm devices approach the length of pentacene (~1.2 nm). Transport at low temperature is via tunneling as evidenced by the temperature-independent electrical characteristics at $T = 4$ and 2 K (Figure 2d). Though not fully understood, the steplike features in the low-temperature $I_{ds} - V_{gs}$ data (Figure 2d) have been observed with multiple samples and could be related to tunneling currents through discrete molecular orbitals of pentacene.

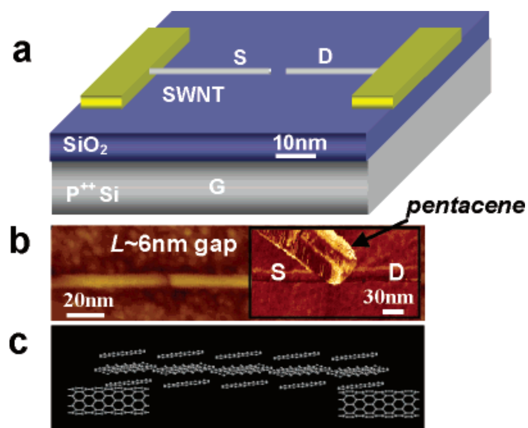

Figure 1. SWNTs as electrodes for small organic FETs. (a) Schematic drawing of a cut SWNT with a sub-10 nm gap to be used as source (S) and drain (D) electrodes of an organic FET. The doped Si serves as a back gate (G), and the SiO_2 thickness $t_{ox} = 10$ nm. (b) AFM image of a cut SWNT (diameter ≈ 2 nm, gap size L measured to be ~6 nm after correction of the tip size effect). Right inset: AFM image of a vapor-deposited pentacene crystallite bridging a cut SWNT (see Supporting Information). (c) Drawing of a pentacene crystallite bridging two SWNT electrodes.

For comparison with SWNT-contacted devices, we fabricated short organic FETs with conventional metal electrodes using electron beam lithography on similar $t_{ox} \approx 10$ nm SiO_2/Si substrates. The metal electrodes were ~30−40 nm wide and ~20 nm tall (Pd, with ~1 nm of Ti adhesion layer) with a nanogap of $L \approx$ sub-10 nm (Figure 3b inset). Though we were unable to deposit pentacene crystallites to bridge the $L \approx$ sub-10 nm metal gaps because of the poor nucleation of pentacene crystals on the metal electrode, solution dip-coating reliably produced $L \approx$ sub-10 nm long P3HT FETs with both SWNT and regular metal contacts. SWNT-contacted P3HT FETs exhibited 3 orders of magnitude higher current modulation (I_{max}/I_{min}) than the metal contacted devices (Figure 3a vs 3b) over the same $V_{gs} = -2$ to 2 V gate range. The metal-contacted FET can hardly be switched by the gate with a subthreshold swing of $S \approx 4$ V/decade, while $S \approx 400$ mV/decade for the SWNT contacted FET under similar bias voltages of $V_{ds} \approx$ 0.3 V.

The significantly improved switching characteristics of the short organic FETs with SWNT electrodes over those with metal

10.1021/ja045900k CCC: $27.50 © 2004 American Chemical Society

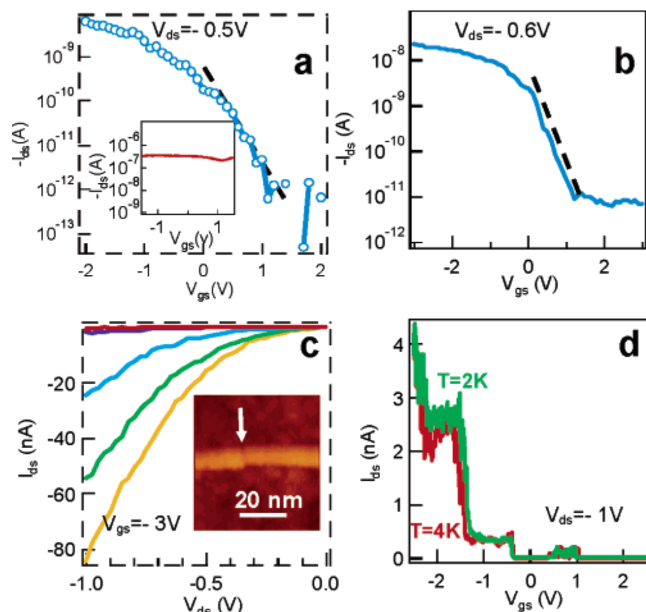

Figure 2. Miniature pentacene FETs with metallic SWNTs as source and drain electrodes. (a) Room temperature (T) current (I_{ds}) vs gate-voltage (V_{gs}) characteristics of a device (channel length $L \approx 6$ nm, tube diameter $w \approx 2$ nm). The dashed line highlights the subthreshold region with $S \approx 400$ mV/decade. Inset: $I_{ds} - V_{gs}$ (recorded under bias = 10 mV) for the metallic SWNT before cutting. (b) Room temperature $I_{ds} - V_{gs}$ characteristics of a $L \approx 1-3$ nm long pentacene device. $S \approx 500$ mV/decade indicated by the dashed line. (c) Room temperature $I_{ds} - V_{gs}$ curves for the device in (b) recorded at $V_{gs} = -3, -2, -1, 0$, and 1 V. Inset: an AFM image of the SWNT after electrical cutting and prior to pentacene deposition. The gap is not fully resolved by AFM. The arrow points to the location of a linelike cut. (d) $I_{ds} - V_{gs}$ curves (at $V_{ds} = 1$ V) for the same device as in (b) and (c) at $T = 4$ and 2 K.

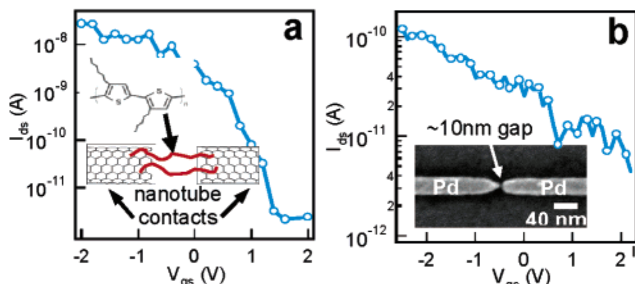

Figure 3. Ultra-short organic transistors ($L \approx 5-10$ nm) with SWNT contacts and conventional metal contacts, respectively. (a) Room temperature $I_{ds} - V_{gs}$ characteristics for a P3HT FET with SWNT electrodes ($V_{ds} = -0.2$ V). Diameter of SWNT $w \approx 2$ nm, and the gap in nanotube $L \approx 5-6$ nm. $S \approx 400$ mV/decade. (b) I_{ds} vs V_{gs} characteristics ($V_{ds} = -0.4$ V) for a P3HT FET with metal (Pd) electrodes with $S \approx 4$ V/decade. The inset shows an SEM image of the electrodes (width $w \approx 35$ nm, thickness ~20 nm, gap size ~5-10 nm) used to deposit P3HT and afford the device.

electrodes are attributed to the excellent electrostatics attainable with the nanotube electrode geometry. It has been shown theoretically that for transistors involving Schottky barriers (SB) at the contacts (which is the case for organic devices), sharp quasi-1D geometry of the source (S) and drain (D) electrodes can facilitate the optimum gate control.[4,5,7,8] Because of the small S/D electrode size, the gate electric field will be able to reach into the channel and regions proximal to the S/D contact junctions to suppress the SB for high ON states and to turn OFF the devices efficiently by creating a large body barrier. In contrast, electrostatic gating is ineffective in ultra-short FETs with bulky metal S/D electrodes because of screening of the gate electric fields by the S/D electrodes. Also, the drain potential will be easily penetrating into and dominant over the channel potential, preventing efficient ON and OFF device switching, as seen in Figure 3b.

The electrostatic gating control can be parametrized by a gate efficiency factor $\alpha = C_G/(C_G + C_S + C_D)$ where C_G, C_S, and C_D are gate, source, and drain capacitances to the channel, respectively. The organic devices with SWNT contacts exhibit $S \approx 400$ mV/decade > $(k_BT/e)\ln(10) \approx 60$ mV/decade at $T = 300$ K, suggesting that α is still far from unity and that further enhancement in C_G relative to C_S and C_D is needed. The gate insulator in our current devices is unoptimized and thicker than the channel length. It will be feasible to integrate high κ dielectrics such as ZrO_2[9] into SWNT-contacted molecular FETs to afford ~10-fold increase in C_G and therefore further enhance the electrostatic gate control. With quasi-1D contacts, gate scaling could allow for organic transistors approaching the limit of $S \approx 60$ mV/decade.[10]

It is now feasible to fabricate molecular FETs with molecular width to go with the molecular channel length by using SWNTs as electrodes. With quasi-1D SWNT source and drain, scaling could become meaningful to enhance the performance of organic FETs. It is necessary, however, to form parallel arrays of separated organic devices for high transconductance and currents. Efficient electrostatic gating afforded by quasi-1D electrodes could also facilitate fundamental elucidation of transport in molecules by accessing electronic orbitals within wide energy windows. The intrinsic physical properties of SWNTs could also be utilized for novel contacts. It has been suggested that even with ideal gating ($\alpha \approx 1$), a limit of $S \approx 300$ mV/decade could exist for molecular transistors with metal (e.g., Au) contacts due to metal-induced gap states resulting from metal-molecule interaction.[4] The relatively low density of states of SWNTs may circumvent this problem. Covalent contacts to molecules could also be made via C-C bonding to the nanotube ends. Further, semiconducting SWNTs as electrode contacts could give functions and properties for devices that differ from metallic electrodes. Last, it should be possible in the future to develop ultra-small gate electrodes to integrate with SWNT source and drain and achieve various molecular devices with molecular sizes in all dimensions.

Acknowledgment. We are grateful to Professor Mark Lundstrom, Jing Guo, Professor Supriyo Datta, and Dr. Avik Ghosh for insights. This project was supported by the MARCO NST Center, DARPA, and an SRC Peter Verhofstadt Graduate Fellowship.

Supporting Information Available: Device fabrication, gap formation in SWNTs, and bridging gaps by organics. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA045900K