Electrical properties and devices of large-diameter single-walled carbon nanotubes

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Individual large-diameter (~3 to 5 nm) semiconducting single-walled carbon nanotubes (SWNTs) are found to exhibit ambipolar field-effect transistor (FET) behavior, with easily accessible *n*- and *p*-conduction channels by simple electrostatic gates. The effects of temperature and ultraviolet radiation on their electrical properties are elucidated, shedding light into the intrinsic behavior of SWNTs in this relatively large-diameter regime. The ambipolar SWNT-FETs can be readily used as building blocks for functional nanoelectronic devices such as voltage inverters that operate under ambient conditions. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1448850]

The interest in electronic and opto-electronic devices beyond the size scale of current semiconductor processing capabilities has fueled a tremendous amount of research in nanoscale materials and molecular electronics.[1] Single-walled carbon nanotubes (SWNTs) are chemically derived wires with atomically well-defined one-dimensional structures. Nanotubes provide new model systems for basic scientific studies and pathways to nanoscale devices. The electrical properties of SWNTs depend critically on diameter and chirality, which is intriguing in terms of basic property–structure relationships and a wide range of possibilities in nanoscale devices.

It is well established that individual semiconducting SWNTs behave as field-effect transistors (FETs), with an orders of magnitude change in the electrical conductance under a varying electrostatic gate voltage. The SWNT-FETs typically exhibit unipolar *p*-type characteristics under ambient conditions due to charge transfer between nanotubes and adsorbed oxygen molecules.[2] Chemical doping, either by charge transfer from alkali metals[3] or by adsorption of electron-donating organic molecules,[4] can lead to *n*-type SWNT-FETs. These devices, however, are typically limited to only one type of carriers in either *p*- or *n*-channel over a large span of gate voltages. The ability to alter the majority charge carriers from electrons to holes and vice versa by simple gate manipulation, and thus obtain ambipolar SWNT-FETs is highly desirable for complex functional devices[5] by integrating nanotube FETs. In this regard, Dekker and coworkers recently have placed electrostatic gates a few nanometers from SWNTs and obtained ambipolar *p*- and *n*-FETs by tuning the gate.[6]

Here, we report the electrical properties of semiconducting SWNTs with relatively large diameters in the range of 3 to 5 nm, and show that they are excellent ambipolar FETs, functional in ambient environment under simple gates. Further, we show that these FETs can be readily integrated into useful nanoelectronic devices by building a voltage inverter. The results are of fundamental interest since the electrical properties of nanotubes with diameters in the 3–5 nm range are addressed for the first time. SWNTs and multiwalled carbon nanotubes have typical diameters on the order of 1 nm and 10 nm, respectively, leaving a gap in between averaged around the 3–5 nm regime that has not been systematically explored previously. In fact, interesting phenomena have already been reported previously with ~3 nm diameter semiconducting SWNTs. These nanotubes exhibit ambipolar behavior but typically with a lower conductance in the *n*-channel than in the *p*-channel.[7,8] Ambipolar behavior has been observed in small diameter (1–2 nm) SWNT-FETs with efficient proximal gates,[6] but these samples also exhibit low *n*-channel conductance.

SWNTs are synthesized by chemical vapor deposition (CVD) of methane [99.99%, flow rate of 100 sccm in a 1 in. furnace with hydrogen co-flow rate 350 sccm and temperature 1000 °C] on patterned SiO_2/Si substrates.[9] The heavily doped Si substrate under a 500 nm thick SiO_2 layer is used as the gate. Importantly, previous, CVD growth at 900 °C have typically yielded nanotubes with diameters ~2 nm or smaller yet, we recently found that appreciable amounts of SWNTs with diameters >3 nm are grown at 1000 °C.[10] The higher growth temperature leads to higher reactivity of methane and, therefore, a more efficient carbon supply, which allows larger catalyst particles to be saturated by carbon and, consequently, the growth of larger diameter SWNTs.[10]

A ~4 nm diameter individual SWNT device exhibiting ambipolar FET behavior is shown in Fig. 1(a). The current versus gate voltage ($I-V_g$) characteristic clearly shows an accumulation (hole transport) region for $V_g < -8$ V, undergoing an insulating region (with three orders of magnitude lower conductance) and switching to the inversion (electron transport) region for $V_g > -4$ V. The transconductance, dI/dV_g, is similar for both modes in the linear $I-V_g$ regimes and gives rise to relatively high mobility of 220 $cm^2/V\,s$ and 150 $cm^2/V\,s$ for holes and electrons, respectively.[11] Ambipolar behavior can also be observed from the $I-V$ characteristic of the device [Figs. 1(b) and (c)]. The resistance of the sample is on the order of 1 M Ω in both the *p*- and *n*-regions, much lower than that for the ambipolar tube FETs made with proximal gates.[6]

Temperature dependent measurements of the $I-V_g$ characteristics reveal that the conductance of the SWNTs-FET

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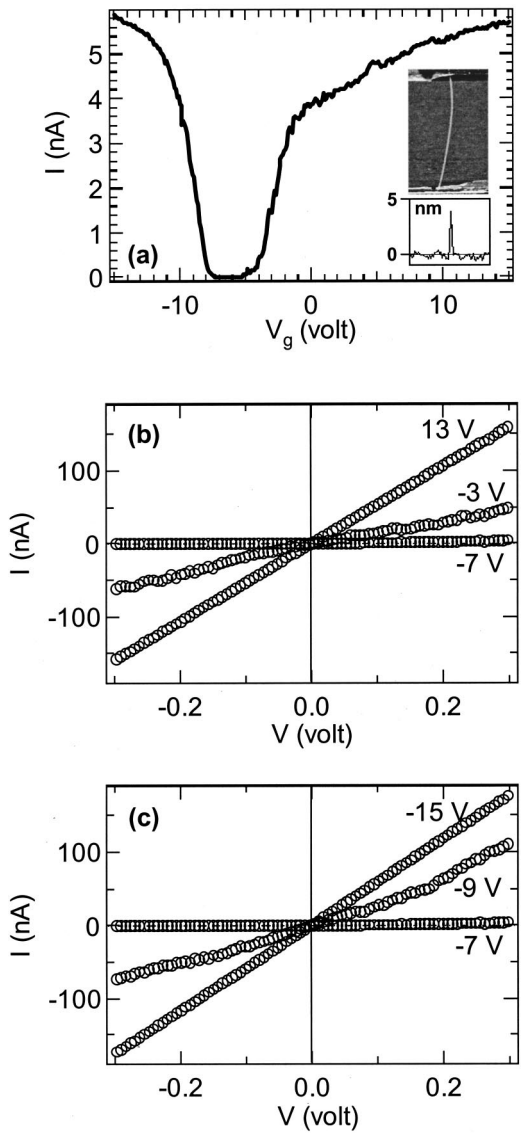

FIG. 1. Electrical properties of an ambipolar SWNT-FET: (a) $I-V_g$ curve measured at 10 mV bias. The lower right-hand side inset is an atomic force microscope image (1.5×3 μm) of the actual device along with its topography height spectrum. $I-V$ characteristics under *n*-channel (b) and *p*-channel (c) modes. The numbers are the corresponding gate voltages.

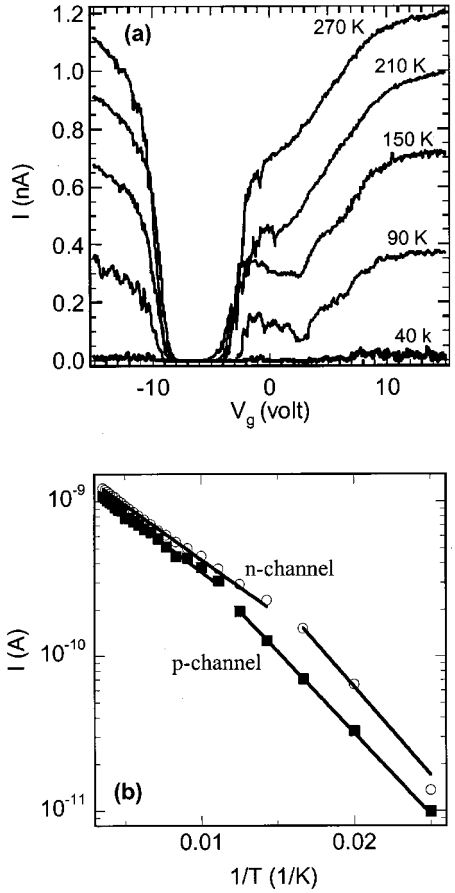

FIG. 2. Temperature dependence of transport properties of an ambipolar SWNT-FET: (a) $I-V_g$ curves at different temperatures measured at 2 mV bias. (b) I vs $1/T$ curves for accumulation (filled squares) and inversion (open circles) modes. The current values for each temperature represent the current average at the linear regions of the $I-V_g$ curves for the *n*-channel (13.5 to 15 V) and the *p* channel (-13.5 to -15 V). The lines are the exponential fits. Two distinct exponentials are required to fit each curve.

decreases monotonically at lower temperatures for both the accumulation and inversion regions [Fig. 2(a)]. At a fixed gate voltage, temperature dependence of the SWNT conductance can not be strictly fit into thermal activation form with a single exponential.[7] Two exponentials appear to fit in two temperature regions. For the *p*-channel, the thermal activation barrier to hole transport is 14 meV for $T>70$ K and 23 meV for $T<60$ K. For the *n*-channel, the barrier for electron transport is 15 meV for $T>90$ K and 21 meV for $T<80$ K. These energy barriers are estimated from the slopes of the current (log scale) versus $1/T$ curves in Fig. 2(b). The origin of the two activation regions is unclear and requires further investigation. These results point to thermal activation as the main mechanism for carrier transport at room temperature. The low energy barriers ($<kT$ at 300 K) for both electrons and holes are highly desired for ambipolar SWNT-FETs with equivalent conductance levels for the *p*- and *n*-channels.

The ambipolar FET characteristics are direct results of the intrinsic electronic properties of large-diameter SWNTs with small band gaps ($\sim$1/diameter). A semiconducting nanotube with diameter $\sim$1.4 nm has a band gap of 0.6 eV,[12] and exhibits *p*-type FET behavior under ambient conditions due to O_2 adsorption. To crossover to the *n*-type region, sufficiently high gate voltages are needed to electrostatically shift down the conduction band[8] of the SWNT by $\sim$0.6 eV. Such a shift, however, introduces large band bending at the nanotube–metal junctions for small-diameter tubes, causing high barriers for electron transport in and out of the nanotube. This is the reason that for typical $\sim$1–2 nm diameter *p*-type SWNTs, one rarely observes appreciable electron conduction even under extreme positive gate voltages. Band bending should also be in effect in the proximal-gate case, as the *n*-channel conductance appears to be two orders of magnitude lower than that of the *p* channel.[6]

On the other hand, larger-diameter semiconducting SWNTs have smaller band gaps. Therefore, smaller band shifts and band bending at the contacts allow significant carrier transport through both the conduction and valence bands, leading to the observed ambipolar SWNT-FET behavior. A gate voltage change, ΔV_g, of $\sim$4 V (gate 500 nm away from the tube) is capable of switching the sample from *p* type to *n* type for the $\sim$4 nm diameter SWNT in Fig. 1. The band gap of the nanotube is estimated to be on the order of $\sim$0.2 eV ($\sim\alpha\Delta V_g$, where $\alpha\sim0.05$ is the typical gate efficiency factor), consistent with theoretical predictions.

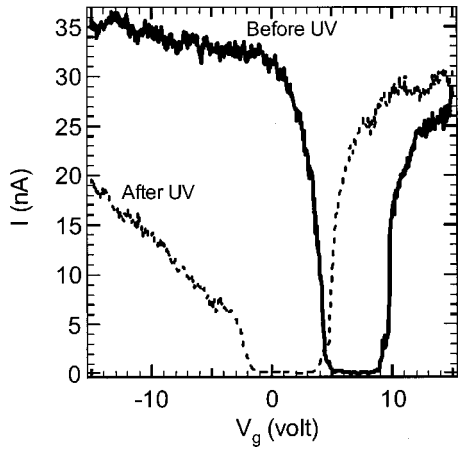

FIG. 3. $I-V_g$ curves of an ambipolar SWNT-FET before and after exposure to 250 nm UV light. Both $I-V_g$ curves are measured at 10 mV of bias voltage.

It has recently been revealed that UV radiation induces molecular photodesorption from SWNTs.[13] Here, we use UV radiation as an effective method of removing O_2 from the large-diameter SWNTs. The depletion region of an ambipolar SWNT-FET, shown in Fig. 3 (solid line), lies between $V_g=5$ and 9 V under ambient conditions. After UV exposure (250 nm and intensity $\sim$0.6 mW/cm^2) for 3 min in an Ar atmosphere, the $I-V_g$ curve of the sample exhibits a -6 V shift as shown in Fig. 3 (dashed line). This confirms the hole-doping effects[14] of O_2. Importantly, both the accumulation and inversion FET modes remain after cleaning O_2 from the tube, which strongly suggests that the ambipolar behavior is characteristic to the relatively large diameter SWNT rather than an effect that arises due to doping by chemical species. Chemical effects do lead to shifts of the $I-V_g$ curve along the V_g axis. Notably, the data shown in Fig. 1(a) where the SWNT exhibits *n* conduction at zero gate voltage (as opposed to the typical *p* conduction in air) should be related to such chemical effects (e.g., incomplete O_2 adsorption on the nanotube).

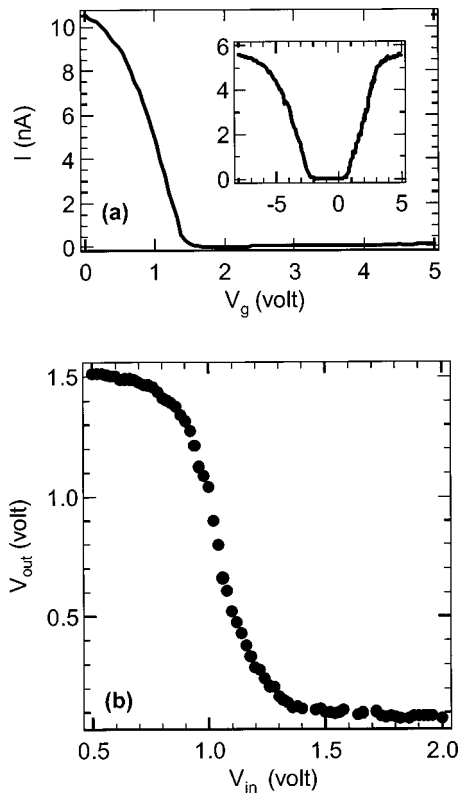

FIG. 4. Characteristics of an intermolecular logic gate built by connecting an ambipolar and a *p*-type SWNT-FETs. (a) $I-V_g$ curve for the *p*-type FET. Inset: $I-V_g$ for the ambipolar FET. Bias=10 mV. (b) Transfer properties of the inverter at 1.5 V of applied bias. The *n*-channel of the ambipolar FET is used as the driver for the *p*-type FET. A gain greater than 1 is obtained.

We have reproducibly observed ambipolar FET characteristics with nine independent semiconducting SWNTs with diameters in the range of 3–5 nm. The ambipolar SWNTs can be used to build functional nanoelectronic devices. For instance, by connecting individual SWNT-FETs, we readily obtain voltage inverters that operate under ambient conditions. Figure 4 shows the transfer characteristic of an inverter with a gain of greater than 1 constructed with an ambipolar and a *p*-type SWNT-FETs fabricated on the same substrate.

In conclusion, we have shown that SWNTs with relatively large diameters exhibit pronounced ambipolar FET behavior with both *n*- and *p*-channels easily accessible by simple electrostatic gates. We have also investigated the effects of temperature and UV-light exposure and found that the ambipolar characteristics are intrinsic to the nanotubes. Also, a voltage inverter is demonstrated by integrating an ambipolar nanotube FET. These results are of fundamental interest in terms of property–structure relations, and may find important applications in nanotube based molecular electronics.

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