

Conductance measurement of single-walled carbon nanotubes in aqueous environment

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We report measurement of conductance of single-walled carbon nanotubes in aqueous media using a field effect geometry in which source and drain electrodes are protected with a photopolymerized epoxy. Without this protection, exposure to aqueous media degrades the device instantly. The 2.6 μm width open slits are prepared by photolithography at the central region between source and drain electrodes, whose spacing, or channel length, is 5 μm , so that only the nanotube channel can be directly exposed to an aqueous environment, while the metal–nanotube junctions are protected. For protected devices, the response to water as characterized primarily by changes in threshold voltage is reversible and reproducible. © 2003 American Institute of Physics. [DOI: 10.1063/1.1566084]

Carbon nanotubes^{1,2} possess many attractive properties required for chemical sensing in the nanometer regime. In particular, field-effect transistors (FETs) of semiconducting nanotubes^{3–7} are suitable for sensor applications since they are known to exhibit charge-sensitive conductance. Nanotube FETs have been used in gaseous phase sensing by Kong and his co-workers.⁸ Many sensor applications, such as those involving biological analytes, require aqueous solutions. Recently nanotube FETs have been shown to work in a sodium chloride solution^{9,10} where an electrolyte solution is used to form the gate electrodes. However, water is often detrimental to both organic and inorganic semiconductor devices. Nanotube FETs are not an exception, as will be demonstrated in this work. Thus, it is very important to establish a reliable scheme to measure conductance of carbon nanotubes in the presence of water on a reasonably long time scale.

In this work, we have fabricated single-walled carbon nanotube FETs incorporating a electrode protection scheme and we report measurement of conductance of nanotubes under aqueous environment in a field-effect transistor geometry. Carbon nanotubes are synthesized by chemical vapor deposition (CVD) on patterned substrates¹¹ and electrodes are formed using shadow mask techniques. We find in nanotube FETs that water-mediated degradation of device performance occurs mainly at or near the contact regions, which can be avoided or minimized by coating source and drain electrodes with a hydrophobic photoepoxy. The 2.6 μm width open slits are prepared by photolithography at the central region between source and drain electrodes. When only nanotube channel is directly exposed to water droplets, we find that the device responds to water by a reversible and reproducible change in the threshold voltage.

The cross section of the device structure is schematically

shown in Fig. 1(a). Single-walled carbon nanotubes are synthesized by atmospheric-pressure CVD on the patterned substrates, a method that originally was developed by Dai and his co-workers.¹¹ The preparation of catalyst patterns is very similar to the method described in Ref. 11. The heavily doped Si substrates capped with 100-nm-thick SiO_2 are coated with 300-nm-thick poly(methylmethacrylate) (PMMA) (MicroChem, A5.5) and exposed to an excimer laser (KrF, $\lambda = 248$ nm, 20 mJ/pulse, 20 Hz) through a quartz lithographic mask for 4 min followed by development. Alumina-supported Fe/Mo catalyst material suspended by methanol is spun on the substrates followed by lift-off in acetone to form thin catalyst islands nominally 4 μm in diameter with a periodicity of 18 and 50 μm in x and y directions, respectively. The substrates with catalyst islands are loaded into a quartz tube (1 in. in diameter), heated to 850 °C, and maintained for 30 min under 1 l/min of argon and 100 ml/min of hydrogen, followed by CVD growth for 4 min at the same temperature under 500 ml/min of argon, 50 ml/min of hydrogen, and 500 ml/min of methane.

Immediately after removing the nanotube-bearing substrates from the CVD system, metal shadow masks are placed on the substrates. The assemblies are then loaded into a conventional vacuum evaporator system to form source (S) and drain (D) electrodes consisting of a 5-nm-thick chromium adhesion layer and a 25-nm-thick gold contact. The metal shadow mask consists of two components: fine tungsten wires (Sigmund Cohn Co. Ltd.) whose diameter is 5 μm ¹² and nickel sheets (20 μm thick) containing 50 $\mu\text{m} \times 2$ mm slits with a spacing of 50 μm made by an electroforming method, a kind of nickel plating (Kyosei Co. Ltd., Japan). In this way, the gap size between S/D electrodes (i.e., the channel length of FET) is precisely determined by the diameter of fine tungsten wires. The present resist-free process allows us to consistently obtain good contact resistance without annealing. The typical two-probe resistances of

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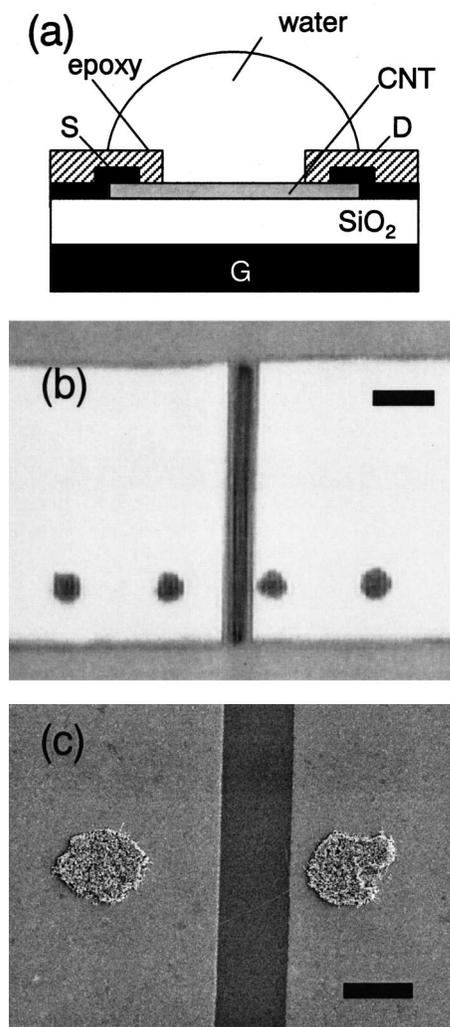


FIG. 1. (a) Schematic structure of a nanotube FET. The source (*S*) and drain (*D*) electrodes are covered by a photoepoxy (protection layer). (b) An optical microscopic image of a nanotube FET with protection layer. A $2.6\ \mu\text{m}$ width open slit is prepared between *S/D* electrodes by photolithography. The four dark circles are catalyst islands consisting of alumina-supported Fe/Mo. A scale bar indicates $10\ \mu\text{m}$. (c) A scanning electron microscopy image of a portion of a nanotube FET before a photoepoxy process. One single-walled carbon nanotube bridges *S/D* electrodes. A scale bar indicates $5\ \mu\text{m}$.

semiconducting and metallic nanotube devices are 130 and $50\ \text{k}\Omega$, respectively. The best values obtained in the present method are 75 and $30\ \text{k}\Omega$, respectively.

A photoepoxy is used to form protection layers,¹⁴ which cover entirely *S/D* electrodes. As shown in Fig. 1(b), the $2.6\ \mu\text{m}$ width slits are formed in the central region between *S/D* electrodes by photolithography. The preparation of these protection layers is crucial to useful measurement of conductance of semiconducting nanotubes under the aqueous environment, as will be explained later in detail. A negative photo resist (MicroChem, SU8-2) is coated on the chip at a spinning speed of 3000 rpm to form a $1.5\text{-}\mu\text{m}$ -thick film. The assembly is baked at $65\ ^\circ\text{C}$ for 60 s and $95\ ^\circ\text{C}$ for 90 s, cooled down to room temperature for 10 min to relax the strain of polymer molecules, exposed to UV light ($365\ \text{nm}$, $6\ \text{mW}/\text{cm}^2$) for 1.2 s, baked at $65\ ^\circ\text{C}$ for 60 s and $95\ ^\circ\text{C}$ for 60 s, and developed with SU-8 developer for 45 s, following the manufacturer's recommended procedure. Squares win-

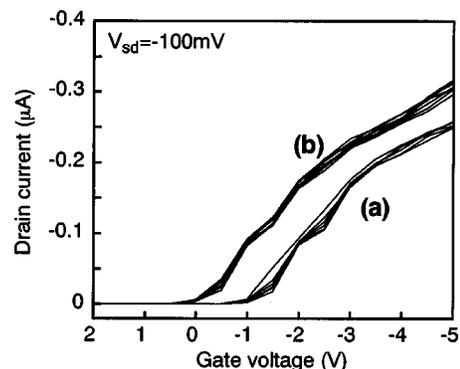


FIG. 2. Drain current measured as a function of gate voltage (a) before and (b) after the nanotube within the FET channel is exposed to water. Six scans are shown for both (a) and (b).

dows ($50\ \mu\text{m} \times 50\ \mu\text{m}$) are also formed so that electronic probes can contact the electrodes.

An issue of concern is process compatibility of the photoepoxy resist SU-8 with nanotube FETs. We do always observe slight changes of FET performance after forming protection layers, primarily reduction of saturation currents, and reduction of threshold voltages. Typically the reduction of current varies from device to device by 10%–80% and in some rare cases the conductance decreases by several orders of magnitude after SU-8 process. These changes may be attributed to strains induced by the polymerization process and/or a change of dielectric constant (ϵ of SU-8: 4)¹⁵ near the contact regions, which could change gate coupling significantly. The former case may be possibly overcome by optimizing the relaxation process and/or with a reduction in the thickness of the SU-8 layers.

The drain currents are measured with a semiconductor parameter analyzer (Keithley 4200) with source-drain bias of $-100\ \text{mV}$ as a function of gate voltage, which is swept from $+2.5$ to $-10\ \text{V}$ in steps of $-0.5\ \text{V}$. Six scans measured in the ambient air are shown in Fig. 2(a). The threshold voltage and transconductance are $-1\ \text{V}$ and $0.1\ \mu\text{A}/\text{V}$, respectively, at gate potential of $-2\ \text{V}$. The saturation current is about $0.65\ \mu\text{A}$ at $V_{\text{sd}} = -100\ \text{mV}$ and $V_g = -20\ \text{V}$, which corresponds to on-state resistance of $130\ \text{k}\Omega$. Then, high-purity water (Aldrich, purity $>99.5\%$, conductance $<2 \times 10^{-6}\ \Omega^{-1}\ \text{cm}^{-1}$) is delivered to the device through a microinjection system with a glass micropipette, which creates droplet of $10\text{--}300\ \mu\text{m}$ in diameter. Corresponding measurements for six scans started at a few seconds after the delivery of water droplet and completed before the droplet had evaporated are shown in Fig. 2(b).

The data of Fig. 2 demonstrate that stable measurements are possible even under conditions where the active channel is exposed to water. The gate voltage dependence of drain currents measured under water looks very similar to those without water although the threshold voltage is changed by $1\ \text{V}$. This response was reversible and reproducible, as will be shown more unambiguously later.

The preparation of protection layers is crucial for measurement of conductance of semiconducting nanotubes under water. Indeed, we observe major deviation from the behavior described earlier for similar devices fabricated without the protection layer upon direct exposure to water.¹⁶ For ex-

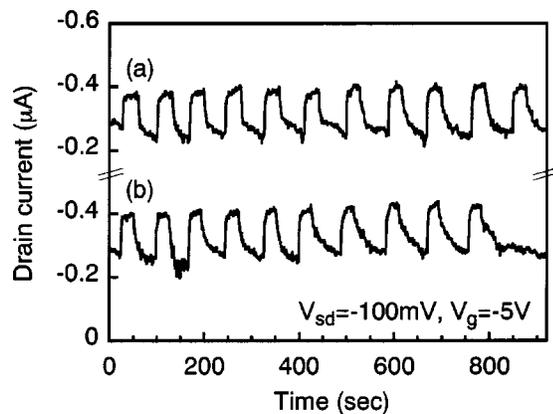


FIG. 3. The measured drain current as a function of time for fixed gate bias of -5 V and source-drain voltage bias of -100 mV. After initial stabilization of the device, the first water droplets are delivered to the device at time $t=28$ s. The droplet vaporizes gradually, disappearing at time $t=62$ s. At time $t=101$ s, a second droplet is delivered and similar responses are observed. This procedure is repeated for 21 cycles. There is an interval of a few seconds between the upper trace (a) and lower trace (b).

ample where the droplet size exceeds several hundreds μm , water-mediated leakage current between S/D electrodes and/or water-associated gate-leakage currents are dominant and measurement of conductance of nanotubes becomes impossible. When water droplets of several tens of microns in diameter are delivered onto unprotected devices, we can avoid leakage mentioned earlier, but we observe that electron transport in the nanotube is quenched: the on-state resistance increases by at least four orders of the magnitude (>1 G Ω). After water vaporizes completely, the quenched conductance recovers gradually to about the half of the initial value after several hours. Another cycle of measurements under water causes further reduction of current. This detrimental effect of water, or conductance quenching, is observed even when voltage biases were set to $V_{sd} = -10$ mV and $V_g = -0$ V. Similarly, the observed conductance is quenched upon application of small droplets of ethanol and methanol. In contrast, nanotube FETs without protection layers operated successfully under several nonpolar or less-polar organic solutions, including dodecane, xylene, and hexane.

We have measured the drain current as a function of time using the same device with an epoxy protection layer. When measurements start with $V_{sd} = -100$ mV and $V_g = -5$ V, the current decreases gradually and reaches steady values of 0.25 μA after several minutes of operation under ambient conditions. After this stabilization of the device, we inject water droplets. Thus at $t=28$ s, the first water droplet is delivered. The drain current increases by 30% and becomes steady, as shown in the upper trace of Fig. 3. As the droplet vaporizes naturally, the current level does not change significantly. At $t=62$ s the droplet disappears, the current suddenly decreases by 25% and then gradually returns to the initial value. At $t=101$ s, a second droplet is delivered and similar responses are observed. The same procedure is repeated for 21 cycles. There is an interruption for a few seconds between the end of the measurement in the upper trace (a) and the beginning of the measurement of the lower trace (b) due to fulfill of the buffer memory of the instrument.

The data of Fig. 3 show that the response to water is

reversible and reproducible. After we measure currents using the same device with applying voltage for more than 1 h, the overall change of current is less than 10%. Thus, our study demonstrates that stable monitoring of conductance of carbon nanotubes in aqueous media can be accomplished through the use of photodelimited polymeric protection layers. These observations may open the door to a range of sensor applications in the nanometer regime with carbon nanotubes.

Although the precise mechanism is not known definitively, we may speculate on the nature of the mechanism for reduction of threshold voltage upon exposure to aqueous media. At least two factors may play a significant role: namely, charge transfer between nanotubes and water or change of gate coupling strength in the presence of water. In particular, since water has large dielectric constant ($\epsilon = 78.5$) and large Debye screening length (~ 1 μm), an enhancement of gate-nanotube coupling might be expected in aqueous environment, which increases penetration of electromagnetic fields into nanotubes. Additional contributions may come from trace ionic impurities in the water and we will report more details of the response of the system in due course.

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¹²A similar method works with fine tungsten wires with diameter of 2.5 μm (see Ref. 13), which is available from Sigmund Cohn. We can etch this wire for further reduction of diameter down to 900 nm using a hydrogen peroxide solution for 50 min at room temperature, which also nicely produced 900 nm width gaps.

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¹⁶We have made nanotube FETs with protection layers made of 300 -nm-thick PMMA or 1.5 - μm -thick photoresist (AZ5214). In case of AZ5214, the conductance quenched instantly, while the device with PMMA showed significant reduction of drain currents by more than 90% within several seconds after delivery of water.