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Semiconducting single-walled carbon nanotubes exposed to distilled water and aqueous solution: Electrical measurement and theoretical calculation

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We fabricate and measure a single-walled carbon nanotube transistor having a liquid-gate electrode. The ratio value of $I_{on}/I_{off}$ is as high as $10^4$, indicating the presence of a semiconducting channel. A passivation layer over the source/drain electrode greatly suppresses the liquid-gate leakage by about three orders of magnitude. The channel currents are noticeably distinct between two liquid samples: distilled water and aqueous solution ($1 \times 10^{-4}$ M NaCl). This biological sensing ability is attributed to the different electrical double-layer capacitances with respect to the bulk part of the channel. The corresponding theoretical calculation is carried out in detail. © 2006 American Institute of Physics.

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Since Iijima\(^1\) discovered the basic carbon nanotube (CNT) structure in 1991, there have been today a large number of research teams worldwide to examine the potentials of the carbon nanotube. It is well recognized that the single-walled carbon nanotubes can be seen as a quasi-one-dimensional conductor\(^2,3\) and can behave in a metallic or semiconducting way depending upon its diameter and chirality.\(^4,5\) The first CNT field-effect transistor (FET) with the experimental input-output transfer characteristics was reported in 1998.\(^6,7\) Since CNT is highly sensitive to a nearby charge, the device can further find such applications as gas sensor.\(^8,9\) The CNT also can exhibit sensitivities to the electrolyte solution via a liquid gate.\(^10\) However, there were few articles in the literature to address electrical properties of the CNTs that are directly exposed to different liquid samples such as the distilled water and aqueous solution. Here we present one such study on a single-walled carbon nanotube FET having a liquid gate, which is fabricated using conventional processes, followed by the theoretical calculation.

A 300 nm thick Si$_3$N$_4$ layer was grown on the silicon wafer, followed by a 100 nm thick titanium (Ti) metal that was sputtered and subsequently patterned as the source/drain electrode. The spacing between the source and drain electrode was 2 $\mu$m. The single-walled carbon nanotubes\(^11\) were immersed in dimethylformamide (DMF) undergoing the ultrasound wave and spread across the substrate. Then an 800 nm thick photoresist (PR) was laid on the wafer and through patterning, a wide slit\(^12\) was created. The photoresist remaining on the source/drain electrode can serve as a passivation layer. By controlling in advance the density of the immersed CNTs, we achieved a single CNT or a CNT bundle bridging the gap as depicted in Fig. 1. A liquid-gate electrode\(^13\) was set up to develop an electrochemical potential in the electrolyte with respect to the CNT surface. A micropipette was employed to place a small ($\sim 1-0.5 \mu$l) electrolyte droplet into the open slit. The measurement setup is schematically shown in Fig. 1.

The measured drain current for CNTs exposed to both the distilled water (resistivity $\sim 18.2$ M$\Omega$ cm) and aqueous solution ($1 \times 10^{-4}$ M NaCl) for a certain device is plotted in

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FIG. 1. (a) The SEM image of the topside of a device with a CNT bundle bridging the gap, which was formed before the photoresist process; and (b) the measurement setup. The source electrode is grounded, the drain electrode is tied to $V_D$, and the liquid-gate electrode is connected to $V_{lg}$. The passivation layer keeps the source and drain electrode from the solution.
electron injection can be expected, meaning the source electrode, a relatively low Schottky barrier in favor of gen molecules from adsorbing on the surface of the drain/tact. In addition, since the passivation layer can prevent oxygen presence of a passivation layer can substantially reduce the magnitude. The inset shows the liquid-gate current in the distilled water case with and without a passivation layer at $V_{lg}$=1.5 V.

Fig. 2 versus drain voltage with the liquid-gate voltage $V_{lg}$ as a parameter (0, 0.3, 0.9, and 1.5 V). Evidently, a change in the liquid material can produce a noticeable change in drain current, especially at high $V_{lg}$. We also obtained similar results for the other device samples. Therefore, the biological sensing ability is confirmed. Indeed, the ratio value of $I_{on}/I_{off}$ in Fig. 2 is as high as $10^4$, indicating the presence of a semiconducting channel rather than a metallic one. This is consistent with the fact that the intrinsic conductance associated with a metallic CNT is a weak function of the liquid-gate voltage.$^{14}$ The above measurement was performed in the presence of a passivation layer over the drain/source electrode. The corresponding liquid-gate current falls below around $10^{-12}$ A in a wide range of drain voltage. For the case of no passivation layer (that is, no photoresist utilized), we obtained the liquid-gate current of order of $10^{-9}$ A as shown in the inset of Fig. 2 for the distilled water case. Hence, the presence of a passivation layer can substantially reduce the liquid-gate leakage current by about three orders of magnitude. In addition, since the passivation layer can prevent oxygen molecules from adsorbing on the surface of the drain/source electrode, a relatively low Schottky barrier in favor of electron injection can be expected, meaning the n-type operation.$^{15}$

Although the drain current level is very low due to conventional manufacturing processes adopted (i.e., Ti metal), the drain current significantly changes as the liquid solution changes as depicted in Fig. 2. Such remarkable change can be attributed to the different electrical double-layer capacitances with respect to the quantum capacitance of the bulk part of the CNTs, rather than the contact counterpart. This argument is consistent with the use of a passivation layer that can prohibit the contact from the water molecule adsorption. The corresponding theoretical calculation is demonstrated below.

To facilitate the analysis, the work is concentrated on the high drain voltage regime over which the effect of the drain-side Schottky barrier can be ignored. The measured conductance of the CNTs at high drain voltages is plotted in Fig. 3(a) versus $V_{lg}$, showing that the threshold gate voltage for CNTs exposed to distilled water is around 0.77 V while for the $1 \times 10^{-4}$ M NaCl solution it is about 0.32 V. When the liquid-gate voltage reaches the threshold value, the conduction band coincides with the Fermi level in the bulk part of CNTs. Above the threshold point, the charge starts to accumulate in the CNTs and turns on the device. To describe different threshold voltages between different liquid samples, a capacitance model in a liquid-gate electrode to underlying bulk channel system, as depicted in Fig. 3(b), is utilized. Here $C_{lg}$ is the electrical double-layer capacitance between CNTs and ions, and $C_{CNT}$ is the quantum capacitance for CNTs. A relevant relation for the undoped carbon nanotubes can readily be established from this equivalent circuit,$^{13}$

$$ qV_{lg} = E_f + q \cdot \frac{Q_{CNT}}{C_{lg}}, \quad (1) $$

where $Q_{CNT}$ is the charge density per unit length and $E_f$ is the Fermi level relative to the middle bandgap energy. The carrier density of CNTs can be written as

$$ Q_{CNT} = \sum_i q \int_{E_i}^{E_{i+1}} D_i(E) \cdot f(E) dE, \quad (2) $$

where $E_i$ is the bottom of the $i$th conduction subband relative to the middle band gap energy; $f(E)$ is the Fermi-Dirac distribution; and $D_i(E)$ is the density of states given by

$$ D_i = \frac{8}{3 \pi a \cdot V_{ppr} \cdot \sqrt{1 - E}} \quad \text{for } E \geq E_i, \quad (3) $$

where $E$ is the electron energy relative to the middle band gap energy; $a$=0.144 nm corresponds to the carbon-carbon bond distance; and $V_{ppr}$=2.5 eV represents the nearest-neighbor overlap interaction energy. As for double-layer capacitance in (1), it is usually treated as an ideal cylindrical capacitance by $C_{lg} = 2 \pi \varepsilon_0 \varepsilon_r / \ln(1 + 2 \lambda_d / d)$, where $\varepsilon_0$ ($\varepsilon_r \approx 80$) is the dielectric constant, $d$ is the carbon nanotube diameter, and $\lambda_d$ is the Debye screening length. For $1 \times 10^{-4}$ M NaCl solution, taking $d=1.4$ nm (for $E_s \approx 0.56$ eV) (Ref. 2) and typically $\lambda_d = 31$ nm, one obtains $C_{lg} = 1.162 \text{nF/m}$. For distilled water, the Debye screening length is about 1 $\mu$m, comparable to the distance from the liquid-gate electrode to CNTs, meaning that the center of the equipotential surface around the double-layer capacitance is unlikely to be located at the cen-
The quantum capacitance prevails in the liquid-gate to CNTs plotted in Fig. 3. $E_f$ saturate. This is consistent with the point B/H$_2$O $E_f$ related to the common one-dimensional subband diagram, respectively, corresponding to three operating points.

Note that in Fig. 2 for $V_{lg}$=0, the drain current for distilled water is almost two times that for aqueous solution. The plausible origin may be that the H$_2$O molecule is stably adsorbed on the CNTs surface (despite low probability at room temperature), causing CNTs operation from $p$ to $n$-type. This means that some charge is transferred from a single H$_2$O to CNTs. We further assume that the distilled water has higher H$_2$O molecule density than aqueous solution; so H$_2$O molecules are likely to be adsorbed on the CNTs, especially for the case of distilled water. We then take a doping level with 0.02 eV for distilled water while keeping undoped Fermi level for aqueous solution. The H$_2$O molecules transfer about 5000e$^{-}$/unit length; that is, each H$_2$O molecule can transfer about 0.03e$^{-}$. If we take the average distance between H$_2$O molecules of about 0.3 nm, the probability for the H$_2$O molecule adsorption is found to be very low ($\sim 10^{-6}$). Thus, the effect of the doping is simply to shift the $V_{lg}$ by 0.02 V for a fixed $E_f$.

We perform electrical measurement of the CNTs exposed to the distilled water and aqueous solution. The biological sensing ability of the fabricated devices and its physical origin have been confirmed. Theoretical calculation is carried out in detail, which can adequately elucidate experimental data and can provide insights such as the positioning of the Fermi level.

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11The single-walled carbon nanotubes with a diameter of 1.4 nm were supplied by Carbon Nanotechnologies Incorporated (CNI).