Alcohol Vapor Sensors Based on Single-Walled Carbon Nanotube Field Effect Transistors

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ABSTRACT

We have measured conductance of single-walled semiconducting carbon nanotubes in field-effect transistor (FET) geometry and investigated the device response to alcoholic vapors. We observe significant changes in FET drain current when the device is exposed to various kinds of alcoholic vapors. These responses are reversible and reproducible over many cycles of vapor exposure. Our experiments demonstrate that carbon nanotube FETs are sensitive to a wide range of alcoholic vapors.

Chemical sensors[1,2] based on carbon nanotubes have recently attracted a great deal of attention. Nanotubes can be expected to exhibit excellent properties as transducers since they have large surface area and are known to exhibit charge-sensitive conductance. For these applications, semiconducting nanotubes play an important role and therefore field-effect transistor geometry[3,4] is very convenient. Indeed, a number of researchers have reported that nanotube transistors are responsive to several gaseous agents.[2] In particular, Hongjie Dai and co-workers have shown that nanotube transistors are very sensitive to NO_2 and NH_3.[2] In addition, the conductance of nanotubes is known to be sensitive to ambient environments, especially to oxygen and/or oxygen-containing gaseous species.[5,6] For practical sensor application, however, it is necessary to investigate and to understand characteristics such as reversibility, reproducibility, sensitivity, and selectivity to various gaseous analytes.

We report here an investigation of the influence of alcohols on the characteristics of FET devices fabricated from single-walled carbon nanotubes. In particular, we have synthesized single-walled carbon nanotubes by chemical vapor deposition (CVD) and have fabricated field-effect transistor (FET) structures with channel lengths of 2.5 μm and 5 μm. For a given applied gate voltage, we have measured the change in drain current which can be observed when the whole device is exposed to alcoholic vapors, causing changes in the observed operating characteristics (threshold voltage and saturation current) of the FET device.

The structure for our FET-based sensor and the corresponding experimental geometry are schematically shown in Figure 1a. Single-walled carbon nanotubes are synthesized by CVD with patterned Fe/Mo catalysts on heavily doped Si substrates capped with 100 nm thick SiO_2. Jing Kong, Hongjie Dai, and co-workers[7] originally developed this approach. CVD growth is carried out in a quartz tube (1 in. in diameter) at 850 °C for 4 min under the flow of mixed gases of 500 mL/min of argon, 50 mL/min of hydrogen, and 500 mL/min of methane. Then, nanotube-bearing substrates are loaded into a conventional vacuum evaporator system with metal shadow masks 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 spacing between S/D electrodes is 2.5 μm or 5 μm. This resist-free process allows us to obtain good contact resistance without annealing. The fabrication procedure may be found in refs 8 and 9 in detail. The specific growth conditions are adjusted so that a single carbon nanotube bridges the S/D electrodes as shown in Figure 1b.

For a specific applied gate voltage, the current flow between S/D electrodes is measured as a function of time using a semiconductor parameter analyzer (Keithley 4200). Our measurements are carried out under flow of dry nitrogen

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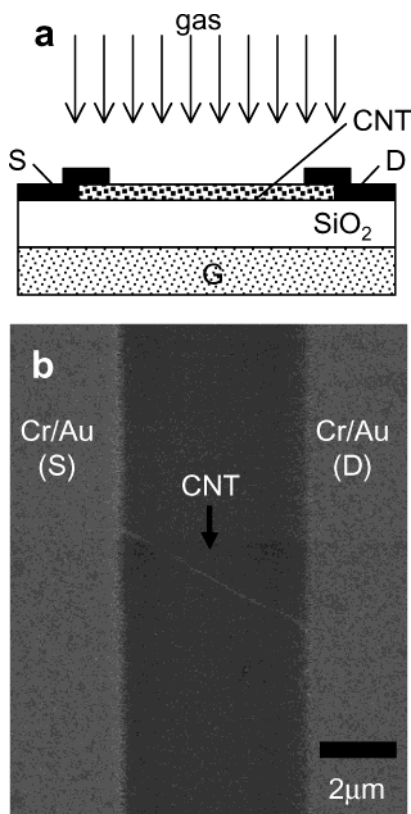§ Department of Chemical Engineering.

Figure 1. (a) Cross-sectional structure of a nanotube field-effect transistor (FET) and the experimental geometry are schematically shown. (b) A scanning electron microscopic image of a part of a nanotube FET. A single-walled carbon nanotube bridges source and drain electrodes with spacing of 5 μm.

Figure 2. (a) Drain current measurements as a function of time with a source-drain bias of -100 mV and a gate bias of -10 V. A typical trace in the controlled experiment and a response to a saturated vapor of ethanol are shown in the dashed line and the solid line, respectively. (b) The responses for 55 cycles of vapor application are illustrated.

with and without addition of saturated or diluted alcoholic vapor. Saturated vapor is prepared by bubbling dry nitrogen through a source solution at ambient temperature, unless otherwise specified. A three-way valve allows the flow of gas to be switched from a pure dry nitrogen source to the saturated vapor source at substantially the same pressure and flow rate. In a typical controlled measurement using dry nitrogen gas, a source-drain voltage of -100 mV, and a gate voltage of -10 V is applied. Figure 2a shows the observed response. Under dry nitrogen flow, the S/D current becomes constant within 1 s after the start of measurement, with fluctuations of about 3% of the average. When the valve system is switched at $t = 0$ s to deliver saturated ethanol vapor to the sensor surface, a sharp spike is first observed after a few seconds and then the current decreases and reaches a steady value. For the specific example of Figure 2a the reduction of the current is about 50%, and this process takes about 10 s. When the measurement is continued under ethanol vapor, no significant change is observed after $t = 10$ s for observations times as long as a few hundred seconds.

If the applied potentials are removed briefly (a few seconds), namely the circuit is open, then restored, and the cycle of dry nitrogen and nitrogen/alcohol repeated, the observed response to ethanol vapor is reproducible and reversible. Figure 2b illustrates current for 55 cycles of vapor application with potential application as described above. The distribution of current at initial values among 55 traces is
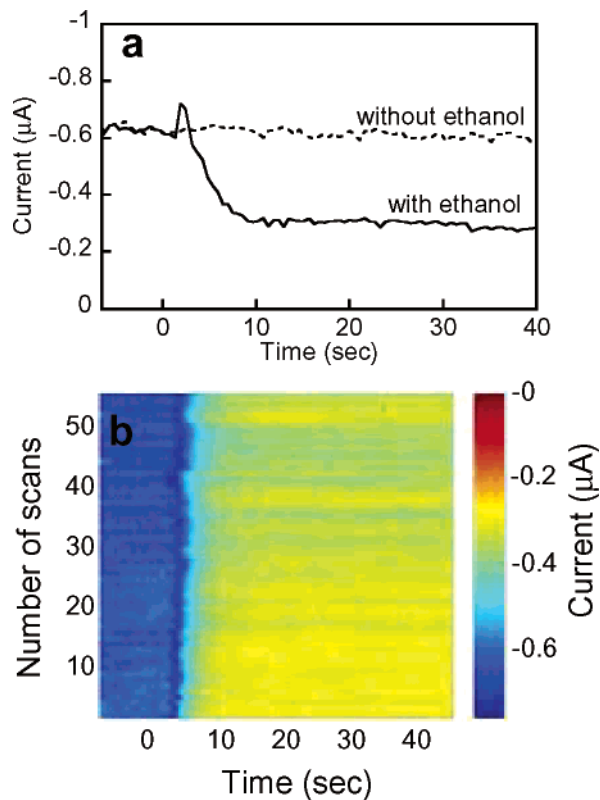
4.1% of the average, while that at the saturated response states is 5.2%, demonstrating excellent reproducibility and reversibility. We observe no degradation in sensor performance in over 1 h of operation; the sensor recovers almost completely after each exposure with recovery time of less than a few seconds. This is short by sensor standards but is significantly longer than the response time of the measurement apparatus. The small observed variations in response time may be primarily due to variations in ethanol injection since the three-way valve is operated manually.

In contrast to the above, when potentials are maintained at fixed values during cycling of exposure atmosphere, we observe that the recovery of current is very slow and that the current level does not return to the initial value, even after tens of minutes at ambient temperature. Thus our experimental data indicate efficient recovery of the sensor device only when voltage biases are released between exposures. Although data are shown only for ethanol in Figure 2, we observe very similar behavior for other alcoholic vapors, as described below in more detail.

We have measured detailed FET characteristics with and without application of ethanol vapor. The dependence of S/D current upon gate voltage is plotted in Figure 3a. For both control and sensing experiments, the S−D voltage was swept from 0 to -100 mV in steps of -20 mV. For the control experiment, a saturated current of -1.1 μA is reached for $V_{sd} = -100$ mV and $V_g = -20$ V, which corresponds to a
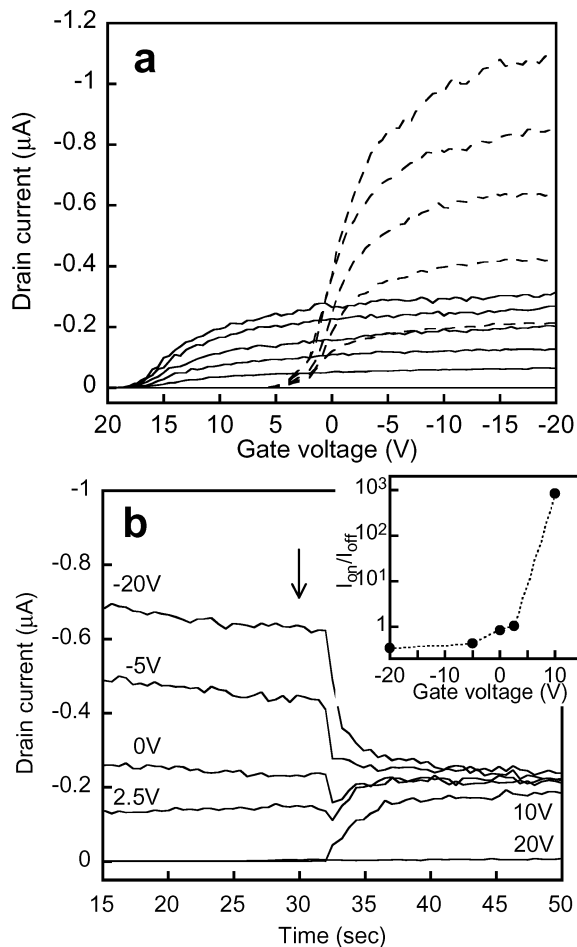
Figure 3. (a) FET characteristics measured with and without application of a saturated vapor of ethanol are shown in the dash line and the solid line, respectively. The S–D voltage was swept from 0 to −100 mV in steps of −20 mV. (b) The responses to a saturated vapor of ethanol were measured with different gate biases as described in the figure. The arrow indicates the time at which alcohol is introduced. The inset shows the ratio of drain current (I_{on}/I_{off}) with and without application of alcohol as a function of gate voltage.

Figure 4. (a) Observed S/D current for $V_{sd} = -100$ mV and $V_g = -20$ V and ethanol vapor with various concentration was applied at $t = 0$ s. The partial pressure of ethanol is 60, 30, 20, 14, 9, 6, 2, and 1 mmHg from the bottom. The inset shows a device response to ethanol as a function of a partial pressure x time, which is a product to evaluate the total dose of ethanol. The partial pressure is shown in the inset. (b) The magnitudes of current reduction at $t = 80$ s are plotted as a function of the partial pressure.

two-terminal on-state resistance of 90 kΩ. This demonstrates that very low contact resistance has been obtained by our shadow mask electrode deposition technique. Over the range of source drain voltages and gate voltages investigated, the observed S/D current scales linearly with applied S/D voltage, showing that the response of the FET device is in the linear regime. A finite drain current is observed at zero gate voltage, which may be ascribed to unintentional doping through CVD growth of CNTs. When similar measurements are carried out under exposure to ethanol vapor, significant changes in FET characteristic are observed as shown in Figure 3a. In this experiment, the threshold voltage changes from 3 to 17 V and on-state current changes from −1.1 µA to −0.32 µA at $V_{sd} = -100$ mV and $V_g = -20$ V. Since measurement takes place in the linear regime, all the traces with vapor application were also scaled well by S–D voltage. However, the data show that the change in current caused by the analytes also strongly depends on gate voltage. Indeed, the S/D current can be increasing, decreasing, or nearly constant by exposure to analytes, depending on gate voltage.
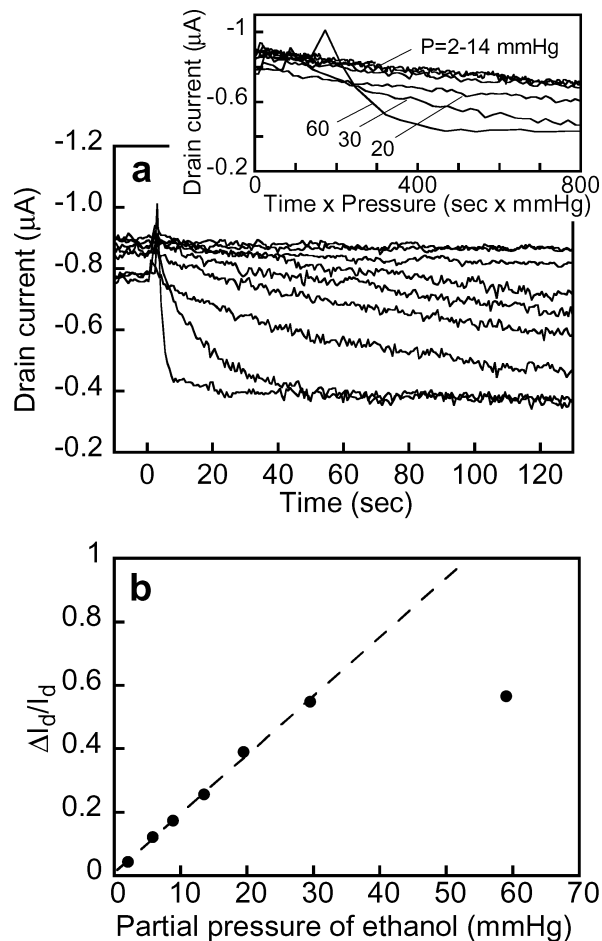
Thus as shown in Figure 3b, we examined S/D currents as a function of gate bias. The observed current decreases at $V_g = -20$ and −5 V when vapor is applied. The current is almost constant at $V_g = 0$ V although a small dip can be seen soon after an application of vapor. It is very interesting to note at $V_g = 10$ V that current increases from almost zero to −0.18 µA. The behavior shown in Figure 3b is quite consistent with the data of Figure 3a. Quantitatively, there is a small discrepancy between the data of Figure 3a and b, which may be ascribed to transient effects in different measurement modes. Measurement with positive gate voltage should be a highly sensitive mode for the sensor device. The inset to Figure 3b shows the ratio of current (I_{on}/I_{off}) with and without application of alcohol as a function of gate voltage. This figure clearly shows that I_{on}/I_{off} increased with increasing V_g and gets maximized at $V_g = 10$ V. The data point at $V_g = 20$ V was not shown in the inset since both I_{on} and I_{off} are very close to the noise level and, therefore, I_{on}/I_{off} is not accurate.

Next, diluted vapor of ethanol is delivered to the device. As shown in Figure 4a, the S/D current at $V_{sd} = -100$ mV

Table 1. Magnitudes of Source-Drain Current Reduction Caused by Various Kinds of Alcoholic Vapors with Voltage Biases of $V_{sd} = -100$ mV and $V_g = -20$ V and Their Partial Pressures[a]

	ethanol	methanol	1-propanol	2-propanol	1-butanol	tertiary-butanol	1-pentanol	1-octanol
ΔI/I %	70	57	93	87	85	91	41	0
P mmHg	126	59	20	47	6.0	75	2.2	0.04

[a] The partial pressures at 34 °C for tertiary-butanol and 25 °C for other analytes are calculated with a formula of $\log P = A + B/T$, where A and B are taken from Ref 12, P is pressure, and T Ii Temperature

and $V_g = -20$ V is monitored as a function of time for application of ethanol vapor of specified dilution. The partial pressure of ethanol was varied from 60 mmHg (a saturated vapor at 295 K) to 1 mmHg. As the partial pressure is reduced from 60 to 30 mmHg, the rate of the current decay decreases but the saturated value remains the same. With further decrease in ethanol pressure, the rate further decreases and the current does not reach a saturated value within a 150 s period of the measurement. As shown in the inset of Figure 4a, the response to ethanol was plotted as a function of the product of partial pressure and time, which is a measure of the total applied dose of ethanol. These data suggest that some first-order physical or chemical process is the dominant mechanism, at least at low ethanol partial pressures. The observed magnitudes of current reduction, $\Delta I_d / I_d$ at $t = 80$ s, are plotted in Figure 4b as a function of the ethanol partial pressure. It may be seen in Figure 4b that the current levels are linearly proportional to the partial pressure in the range of 2 to 30 mmHg. In case of 1 mmHg, the change of current was within 3%, which is below the noise level. Thus, the sensitivity of this device for ethanol in dry nitrogen is about 0.3% (molar fraction). To further increase the sensitivity, reduction of the noise level is very important, and this may be achieved by using a controlled environment inside the chamber. Furthermore, the use of circuit-based sensor techniques can perhaps improve the sensitivity by a factor of 10 or so.[10,11]

We have found that nanotube transistors are also responsive to alcohol vapors of varying chemical composition. Figure 5 shows the observed drain current as a function of time for exposure of the device to saturated vapors of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, tertiary-butanol, 1-pentanol, and 1-octanol starting at $t = 0$ s. All analyte solutions are maintained at 25 °C except for tertiary-butanol, which is heated to 34 °C to increase partial pressure. Table 1 summarizes the magnitude of current reduction and indicates the partial pressures of analytes (but note that in the case of tertiary-butanol, the actual partial pressure may be lower than indicated because of condensation).

For $V_g = -20$ V and $V_{sd} = -100$ mV, the observed response to vapors of methanol, ethanol, 1-propanol, 2-propanol, and tertiary-butanol is rapid and current reduction saturates within 5−15 s. The magnitude of current reduction exceeds 50% for these five analytes and reaches 93% for 1-propanol. When the responses to methanol, ethanol, and 1-propanol are compared, the current levels in the saturation regime depend on the chemical nature of the analytes. This result suggests that identification of alcoholic vapors may be possible without complicated gaseous analysis. In contrast, responses to 1-pentanol and 1-octanol are slow and the
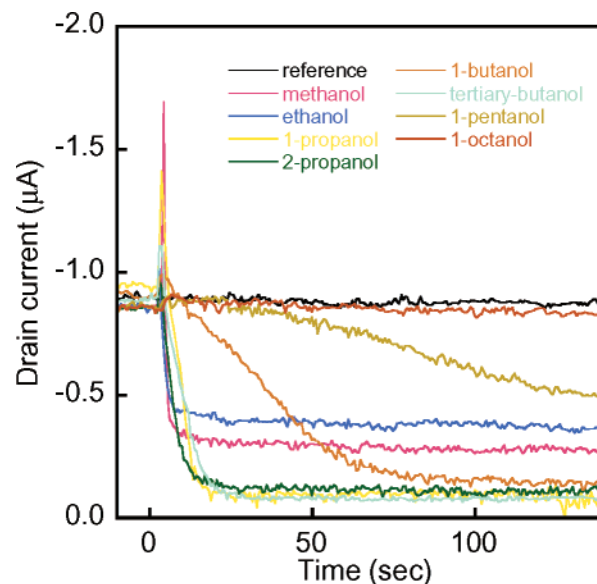

Figure 5. Drain currents for $V_{sd} = -100$ mV and $V_g = -20$ V are shown as a function of time for application of saturated vapor of various kinds of alcohols: methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, tertiary-butanol, 1-pentanol, and 1-octanol.

observed current is still decreasing at $t = 150$ s. 1-Butanol represents a somewhat intermediate case. Although its response time is about 70 s, the magnitude of current reduction is 85%, which is much larger than that of methanol or ethanol. However, it should be noted that the partial pressures of saturated vapors of 1-butanol, 1-pentanol, and 1-octanol are much lower than the other analytes and the slope of current reduction could be correlated to the pressure. In contrast, responses to other analytes with high vapor pressure cannot be explained simply by pressure or dielectric constant. These present results indicate the diversity of sensing response with nanotube transistors. These results are encouraging for the construction of unique gaseous analysis systems in the nanometer regime. We can expect enhanced diversity of response through chemical functionalization of the nanotubes, which allows one to control the chemical binding with particular analytes.

We now consider the possible sensing mechanism of nanotube FETs. In previous studies, different sections of the nanotube have been identified as being relevant for the response of nanotube FET to the environmental condition. Initial studies, such as nanotube FET response to O_2,[5,6] K,[13,14] and NO_2 [2] suggested that bulk doping on the nanotube body is responsible for the change of switching characteristics. However, later study[15−18] indicates that the change of Schottky barriers (SB) induced by gas adsorption at the nanotube/metal contact interface is the dominant mechanism

of change of nanotube FET characteristics, at least in the case of oxygen exposure. In our results above, we note two major findings related with this issue as follows: (i) the nanotube FET can be immediately regenerated by removing the applied potentials with discontinuing alcohol vapor exposure. Note that simply removing vapor without gate voltage change results in a device regeneration time of more than an hour. (ii) Response to the alcohol vapor in different partial pressure can be scaled by the vapor exposure (pressure × exposure time) for low partial pressure of alcohol. The inset to Figure 4a demonstrates that all sensor responses at low partial pressures (<20 mmHg) can be collapsed into one curve. As the alcoholic vapor approaches the saturated pressure, however, the response curve shows a deviation with a transition dip at the beginning of exposure. Based on the first observation, i.e., (i) above, we can rule out the direct effect of alcoholic vapor to the metal/nanotube interface, since the electric field from gate electrode is shielded by the source drain electrode in this region. Therefore, together with (i) and (ii) above, these findings suggest that the sensing mechanism of nanotube FET might be related to electrochemical adsorption or reaction of alcoholic vapors. For example, the adsorption or reaction of the alcoholic molecule could dope the nanotube or it could change the substrate potential by electrochemical adsorption to silicon oxide surface, filling out the charge traps.[18] It also could alter the Schottky barrier at the nanotube−metal interface indirectly by changing the doping level and/or incomplete screening of electrostatic. Further controlled experiments, such as chemical treatment of the silicon oxide surface prior to the gas exposure to control experiments, can possibly elucidate this important issue.

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