

**Full Paper****Sensing with Nafion Coated Carbon Nanotube Field-Effect Transistors**

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Received: June 30, 2003

Final version: August 15, 2003

**Abstract**

Sequential CVD and CMOS processes were used to make a FET that has single walled carbon nanotubes to serve as the conducting source to drain channel. This structure can be decorated to provide gas and liquid responses and herein is evaluated as a humidity sensor. The Na<sup>+</sup>, K<sup>+</sup>, and Ca<sup>2+</sup> ion-exchanged Nafion polymer acts as the chemically sensitive layer in this electrochemical sensor. The effect of gate voltage on the charge-sensitive NT structure was found to be RH dependent over the range of 12–93% RH with msec response time.

**Keywords:** Single-walled carbon nanotubes field-effect transistors (NTFETs), Nafion membranes, Relative humidity sensor

**1. Introduction**

Since they were first made in 1998 [1], field effect transistors made from semiconducting single-walled carbon nanotubes (NTFETs) have been found to be sensitive to various gases, such as oxygen [2], ammonia and nitrogen dioxide [3]. Such devices, together with devices based on nanowires [4], have been explored as chemical [5] and biological sensors [6–8].

We have used the NTFET as the platform for the design of sensitive and selective chemical sensors. We have found that specific chemical functionalization of NTFET devices can make them responsive to a variety of gases, vapors, liquids, and ions. These individually functionalized NTFETs can be used to create large sensor arrays [5], a first step in making chemical and biological detection systems such as electronic noses and tongues [9–11].

Nanotube/polymer systems have recently received much attention for solubilizing carbon nanotubes [12–16]. Polymer coatings have also been shown to functionalize non-covalently bonded carbon nanotubes [17] and modify the characteristics of nanotube FET devices [18]. In particular, polyethylene-imine (PEI) was found to shift the FET device characteristics from p to n-type, presumably due to the electron-donating ability of amine groups in the polymer. Recently, we have exploited another attribute of a polymer coating: the creation of ionic charges on or in the vicinity of the device induced by poly-(sodium 4-styrenesulfonate) [19].

Because of their unique ion-exchange, discriminative, stability, chemical resistance, and biocompatibility properties, Nafion films have been used extensively for the modification of electrode surfaces and for the construction of amperometric biosensors [15, 20, 21]. The humidity dependence of the conductivity of Nafion coated electrodes

has been studied [22, 23] for different ion-exchanged materials. In this paper, Nafion membranes were constructed on the NTFET devices and their effect on the device characteristic is presented. The study of Nafion coated NTFET devices, including their humidity dependence at different membrane compositions is an important first step towards carbon nanotube based RH and biosensors. The commercial viability of Nafion as an ionic polymer membrane and the unique charge sensitivity of the robust NT structure offer an attractive opportunity to investigate a potentially highly reliable RH nanosensor.

**2. Experimental****2.1. Materials**

Nafion 5% (w/w) solution was purchased from Aldrich and was used without additional purification.

For electronic measurements, Nafion was diluted to 1wt.% in 1 mM aqueous solutions of various carbonates (Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, and CaCO<sub>3</sub>). Commercial Nafion is received in the hydrogen ion form with equivalent weight of 1,100. Ion-exchange of the hydrogen ions in the Nafion (~9 mM) with either Na<sup>+</sup>, K<sup>+</sup> or Ca<sup>2+</sup> was achieved by heating the Nafion solution with corresponding carbonate (1 mM) solution.

**2.2. NTFET Fabrication**

Devices were prepared using lithography techniques on 100 mm wafers. Figure 1A shows a schematic diagram of the carbon nanotube devices. NTFET devices were fabricated

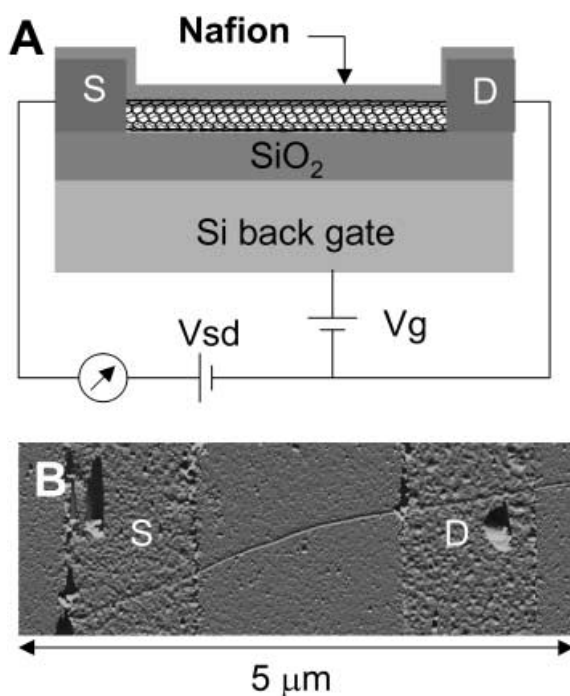


Fig. 1. A) Schematic representation of a field-effect transistor device with a carbon nanotube transducer contacted by two Ti/Au electrodes (source and drain) and a silicon back gate. Carbon nanotube conducting channel is exposed to and covered by the Nafion. B) Atomic force microscope (tapping mode) topograph of the actual nanotube device coated with Nafion.

using SWNTs grown by chemical vapor deposition (CVD) on 200 nm of silicon dioxide on doped silicon from iron nanoparticles with a methane/hydrogen gas mixture at 900 °C. Electrical leads were patterned on top of the nanotubes from titanium films 35 nm thick capped with gold layers 5 nm thick, with a spacing of 0.75 μm between source and drain. The experimental details for the NTFET device fabrication have been published previously [24].

The NTFET devices were functionalized by deposition of one drop of 0.05 wt% Nafion solution using a glass pipette to place the solution directly on the die chip and then blowing the surface dry with high purity nitrogen. This functionalization technique leaves a thin layer (< 10 nm) of polymer material on the device, as observed by AFM (Fig. 1B).

For electronic studies, chips with multiple NTFET devices were wire bonded and packaged in a 40-pin CERDIP package before functionalization with Nafion polymers. Further, we used microspotting to coat NTFET devices in an array with the different Nafion polymers that were either Na<sup>+</sup>, K<sup>+</sup>, or Ca<sup>2+</sup> exchanged, because this allowed us to compare the electronic properties and relative humidity dependence of NTFET devices on the same chip. Microspotting of polymer solutions was done with a commercial micropin (Telechem International Inc.) mounted on an in-house micromanipulator equipped with an optical microscope that allowed for positioning the pin over the NTFET devices (Fig. 2).

### 2.3. Electronic Measurements

Electronic measurements of NTFET devices, such as current flow between S/D electrodes as a function of applied gate voltage, were conducted using a semiconductor parameter analyzer (Keithley 4200). The Nafion functionalized packaged devices were assembled in a flow cell (Fig. 2a) in which air with a specific composition could be introduced to the devices. Relative humidity was measured with thermo-hygrometer (VWR) in the outlet of the flow cell. Air with controlled humidity was generated by bubbling room air through a bubbler equipped with different dilutions of 4M H<sub>2</sub>SO<sub>4</sub>. For low humidity measurements, room air was passed through a column with anhydrous CaSO<sub>4</sub> (Drierite). The intermediate values of relative humidity were achieved by mixing different proportions of dry and humid air with a CSSI 1010 precision gas diluter (Custom Sensor Solutions, Inc., Naperville, IL)

## 3. Results and Discussion

### 3.1. NTFET Devices

In order to investigate the effect of the Nafion membrane as well as the effect of charges inside the membrane on NTFET device characteristics, we have prepared Nafion solutions with three different cations: Na<sup>+</sup>, K<sup>+</sup>, and Ca<sup>2+</sup> (Fig. 2C). The cations were introduced into the Nafion membrane in a controlled way by ion-exchange of the Nafion with corresponding carbonates. The ratio of the hydrogen ion form of the Nafion polymer (9 eq.) to carbonate (1 eq.) was such that no free salts could occur when the ion in the membrane is completely exchanged. Thus all charges are located inside the Nafion polymer matrix.

By comparing the effect of these cations on the electrical response of the NTFET, we provide a comparison of two significant chemical characteristics inside the Nafion membrane. Sodium (Na<sup>+</sup>) and calcium (Ca<sup>2+</sup>) have roughly same cation sizes (0.97 Å and 0.99 Å, respectively), but the charge magnitudes are different by a factor of 2. Potassium (K<sup>+</sup>), on other hand, has larger cation radius (1.33 Å), but the same charge as sodium. If the charge is a major effect on the NTFET device characteristics [19], then Na<sup>+</sup> and K<sup>+</sup> are expected to have a similar effect on the device characteristics, whereas if the ion size is the dominant effect, then the sodium and calcium will be more similar. Of course, the chemistry we expect will be rich therefore, one must consider mobility and hydration sphere among other factors.

Chips with multiple NTFET devices thereon were wire bonded and packaged before functionalization by microspotting with the ion exchanged Nafion polymers. Each of the six NTFET devices on each studied chip were functionalized with a 100 μm size drop of Nafion polymer solution (Fig. 2). Subsequently, the chip was packaged and tested in the flow cell at room temperature.

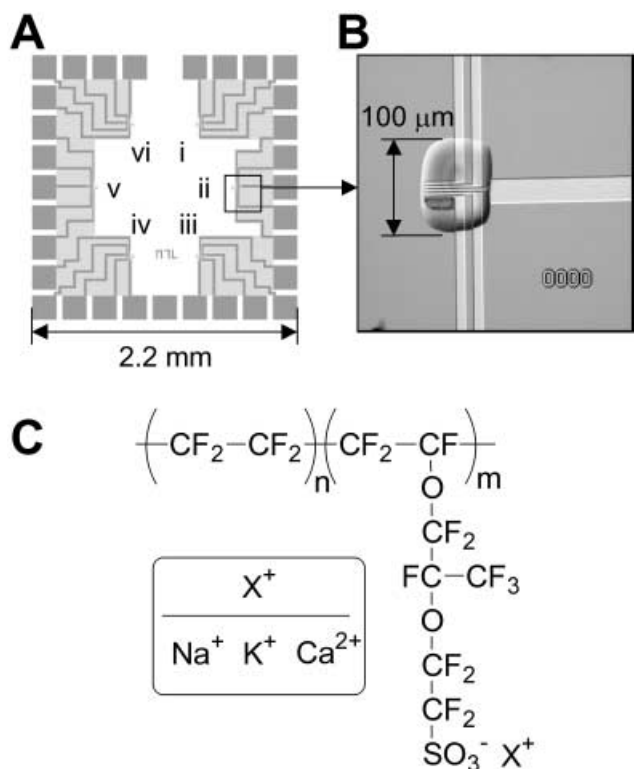


Fig. 2. A) Layout of the chip sensor area with six (i–vi) NTFET devices. B) Optical image showing one (ii) of the NTFET devices after microspotting with a droplet of the selected 1% Nafion solution. C) Chemical structure of Nafion used in fabrication of the array.

### 3.2. Electronic Measurements

The devices discussed in this study contain semiconducting CNTs as the source to drain channel. The dependence of the source-drain current,  $I_{\text{sd}}$ , as function of the gate voltage  $V_{\text{g}}$ , was measured from +10V to –10V. We refer to this response as the IV curve and this curve is used to characterize the device electronics. NTFET devices functionalized with the  $\text{Na}^+$  exchanged Nafion membrane are discussed first. The device IV characteristic before chemical functionalization as well as after Nafion deposition exhibits p-type (Fig. 3A) transistor behavior, presumably due to exposure to oxygen [25, 26] in air. The NTFET modulation (expressed as the ratio of the “on” to the “off” source-drain current, measured at –10 V and +10 V gate voltage respectively) is 1 ( $I_{\text{max}} - I_{\text{min}}/I_{\text{max}} = 1$ ). At low humidity, the hysteresis, i.e., the maximum difference between  $I_{\text{sd}}$  in forward scan +10 V to –10 V and  $I_{\text{sd}}$  in the reverse scan from –10 V to +10 V at a sweep rate of 4 Hz, is around 3 V. The hysteresis increases with an increase in humidity, until it reaches 20 Volts, which is the limit of our device measurement circuit. Figure 3B presents several hysteresis measurements at various relative humidities between 12% and 27% for the devices with  $\text{Na}^+$  ion. The measured hysteresis increases almost exponentially as the humidity increases up to the device measurement limit (20 V).

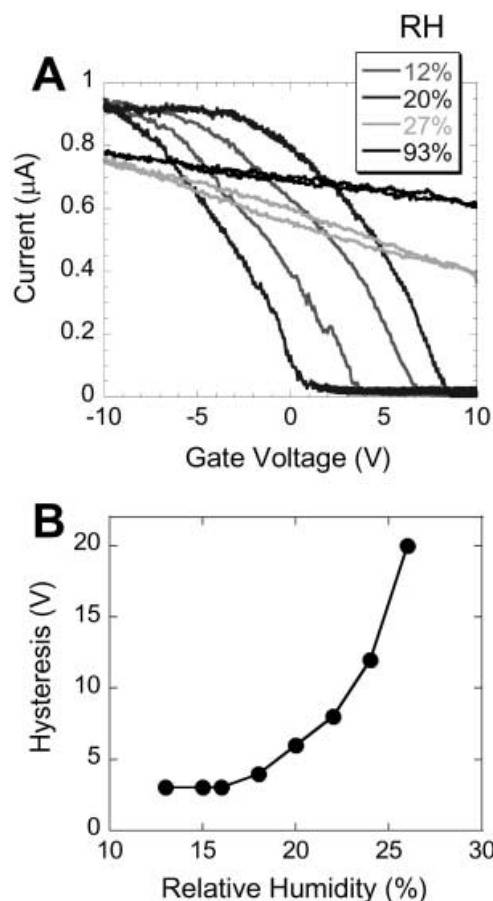


Fig. 3. A) The device characteristics,  $I_{\text{sd}}$  vs  $V_{\text{g}}$  curves ( $V_{\text{sd}} = 40$  mV), of the NTFET device functionalized with Nafion ( $\text{Na}^+$ ) membrane measured at different relative humidity (RH) values. B) Humidity dependence of the reversible hysteresis (forward  $I_{\text{sd}}$  – reverse  $I_{\text{sd}}$ ) in the device measured in the range of 20 volts (–10 V to +10 V) at the sweep rate of 4 Hz.

At higher relative humidity levels, above 27%, modulation of the device becomes smaller than 1 and approaches the limiting value of zero. Therefore we used the modulation of the device as the variable that is strongly dependent on relative humidity. Fig. 4A presents change of the device modulation ( $I_{\text{max}} - I_{\text{min}}/I_{\text{max}}$ ) as a function of relative humidity for the three devices with different ions. Not surprisingly, the functional relationship of the modulation and the RH is unique for each type of cation. Linear correlation with correlation coefficients near unity were obtained (Fig. 4B). The slopes for  $\text{Na}^+$  and  $\text{K}^+$  are quite similar, whereas  $\text{Ca}^{2+}$  is distinctly different with a nearly double the slope and double the charge density. It is the total charge that is responsible for turning “off” the FET character of the nanotubes and  $\text{Ca}^{2+}$  is twice as efficient as  $\text{Na}^+$  or  $\text{K}^+$ . The difference in the cation charge is a logical explanation for this phenomena and it is supported by previous research [19].

We have also performed control experiments with “open” devices. These devices have the exact same geometry as the NTFET devices but have no carbon nanotubes connecting

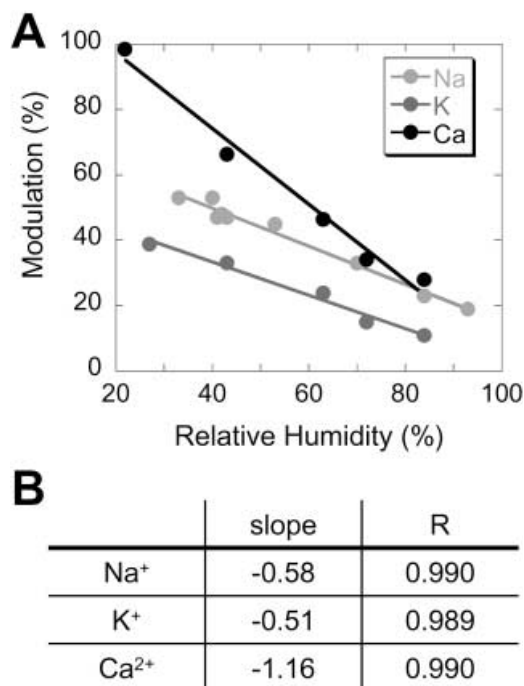


Fig. 4. A) Humidity dependence of the normalized modulation ( $I_{\max} - I_{\min}/I_{\max}$ ) of the three NTFET devices on the same chip functionalized by microspotting with different Nafion ( $X^+$ ) membranes. B) Table of slope and correlation coefficient for each plot.

Ti/Au SD electrodes. Not only is the geometry identical but these devices are on the same chip as the standard NTFET devices. Thus, relative humidity effects on the Nafion membrane deposited by microspotting on the chip with “open” devices can be compared directly with the RH dependence of NTFET devices discussed above. Figure 5A shows source-drain current of the “open” device functionalized with the Na<sup>+</sup> exchanged Nafion membrane at different gate voltages. As expected, the measured  $I_{\text{sd}}$  current was independent of the gate voltage, however, hysteresis was observed depending on the gate sweep direction. Generally, the conductance of the “open” device increases with relative humidity, approaching  $\sim 6$  nS at RH = 93%, which is four orders of magnitude lower conductance than the NTFET device functionalized with same Nafion membrane thickness (i.e.,  $\sim 20$   $\mu\text{S}$ , Fig. 3A). The Ca<sup>2+</sup> and K<sup>+</sup> exchanged Nafion membranes show similar humidity dependence in the roughly same range of conductance as the Na<sup>+</sup> exchanged Nafion (Fig. 5B).

The conductance of Nafion, one of the better ionic conducting polymers, is orders of magnitude different from the same film with carbon nanotubes. Clearly, the RH sensing with the carbon nanotubes is a new and unique mechanism relying on a semiconductor and ionic conductor interface. The Nafion, as the cation (Na<sup>+</sup>, K<sup>+</sup>, or Ca<sup>2+</sup>) is made more mobile at higher RH, is able to react at the NTFET/substrate interface to alter the device performance by effectively shielding the NTFET from the gate voltage. Specific mechanism of the interaction of water at

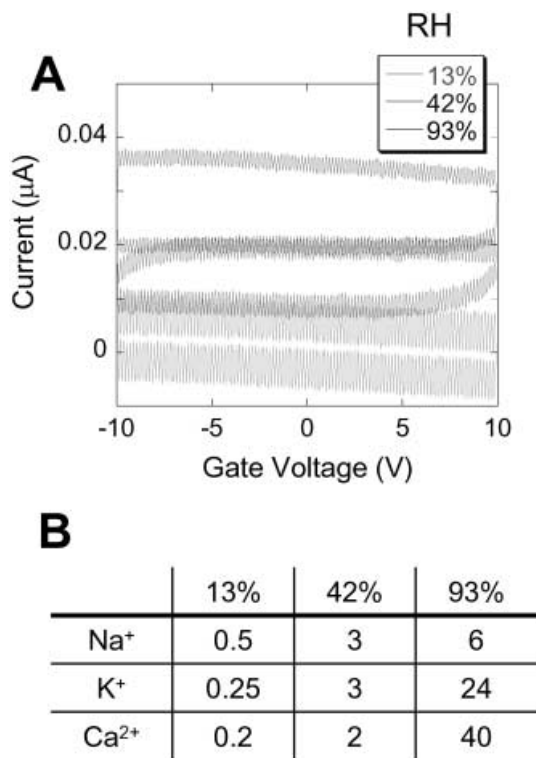


Fig. 5. A) Control measurements,  $I_{\text{sd}}$  vs  $V_{\text{g}}$  curves ( $V_{\text{sd}} = 5$  V), of the “open” device (no carbon nanotubes connecting source and drain electrodes) functionalized with Nafion (Na<sup>+</sup>) membrane measured at different relative humidity (RH) values. B) Table of conductivities (nS) of “open” devices functionalized by microspotting with different Nafion ( $X^+$ ) membranes.

the carbon nanotube/substrate/Nafion interface is under investigation.

#### 4. Conclusions

NTFET devices were functionalized with Nafion membranes in an array geometry on an SiO<sub>2</sub> substrate. We have found that Nafion membranes make the NTFET devices sensitive to humidity and the electronic characteristics of NTFET changes with the magnitude and nature of the ionic charge used in membrane. Many RH sensors designs [22, 23] use direct measurement Nafion conductivity as the active signal. The RH sensor reported here is using the modulation and hysteresis in the conductance of an NTFET by the applied gate voltage. The operation of the back-gated NTFET is not completely understood at this time, but this work provides further evidence [19] that mobile charges shield one or more parts of the NTFET structure from the gate voltage. Future work will investigate specific effects at the source and drain contacts and other important issues.

Microspotting allows several differently responding devices to be constructed on the same chip at virtually no extra cost offering the possibility for tiny arrays with a wide range of useful analytical capabilities. Also, the use of different films with different probe ions in the NTFET configuration

allows the study of ion charge and mobility effects in small nanofabricated devices and on extremely small samples. The NTFET also holds the promise for a tiny mass produced, extremely low power RH sensor that uses thin few-nanometer thick msec-responding films of Nafion. The system should offer exceptional stability since NTs, electrodes, and polymer are extremely rugged and resistant to chemical and environmental exposure.

## 5. Acknowledgements

We acknowledge the Nanomix technical staff for their assistance with device fabrication and measurements. The research was supported partially by NSF SBIR (NSF-0319991).

## 6. References

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