Growth of Nanotubes and Chemical Sensor Applications

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ABSRACT

We have used a number of methods to grow long aligned single-walled carbon nanotubes. Geometries include individual long tubes, dense parallel arrays, and long freely suspended nanotubes. We have fabricated a variety of devices for applications such as multiprobe resistance measurement and high-current field effect transistors. In addition, we have measured conductance of single-walled semiconducting carbon nanotubes in field-effect transistor geometry and investigated the device response to water and alcoholic vapors. We observe significant changes in FET drain current when the device is exposed to various kinds of different solvent. 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 solvent vapors at concentrations in the ppm range.

Keywords: Carbon Nanotube, Single Molecular Sensing, Microfabrication

1. INTRODUCTION

Single-walled carbon nanotubes (SWNTs) are novel molecular scale quantum wires exhibiting many unique properties for potential applications as a building block of nanoscale technology[1]. Among those possibilities, the use of SWNTs as sensor components for chemical and biological detection has been investigated by several groups including ours[2-6]. These initial experiments have demonstrated the possibilities of using SWNT device for sensor applications, by exploiting how sensitive the electronics of the SWNTs are to their electrostatic environment[7-10]. Especially, a mesoscopic, individual SWNT device is widely considered a promising component owing to its extreme sensitivity and electrostatic coupling could yield reliable single electron sensitive events at room temperature [11, 12]. A promising route to high-yield device fabrication is the synthesis of arrays of long parallel SWNTs that can be contacted easily and predictably.

For nanotube sensors from individual tubes, semiconducting SWNTs have been used exclusively since their conductance is highly responsive to the electrostatic coupling and charge transfer from the environment. Dai *et al.*[2] was the first who demonstrated that the electric resistance measurements on semiconducting SWNTs can detect reactive gases, such as NO_2 and NH_3 as they are flowed over the SWNTs. Despite this discovery, the fundamental operating principles of these devices have remained largely unexplored. For example, a recent controversy has emerged regarding the nature of electron transport in semiconducting nanotubes, whether it is dominated by the junctions (presumably Schottky type of metal electrode-semiconducting nanotube) or intrinsic bulk scattering has not been fully resolved. In addition to such confusion, the chemical nature of interaction between various adsorbed molecules and nanotubes is an open issue.

In this paper, we will discuss our recent efforts to grow SWNTs in controlled way to batch fabricated nanotube devices for sensory application. Field Effect Transistors (FETs) were fabricated employing Semiconducting SWNTs between two electrodes and gate electrode underneath the silicon oxide substrate. We observe significant changes in FET drain current when the device is exposed to various kinds of different solvent. These responses are reversible and reproducible over many cycles of vapor exposure. We also present our initial experiments to use nanotubes as nanoscale electrode to use single molecular chemical sensors.

2. SYNTHESIS OF NANOTUBE ARRAYS

Chemical Vapor Deposition (CVD) has proven to be a highly effective method for the production of single-walled carbon nanotubes (SWNTs)[13]. This method involves flowing a carbon feedstock over nanoscale metal catalyst particles at elevated temperatures (typically 800-900 °C, although growth at lower temperatures has been demonstrated). Feedstock gases for this process include methane[14], ethylene[15], CO[15-17] and ethanol[18]; hydrogen is often used to increase growth efficiency. Catalysts include Fe, Fe/Mo, Co, and Co/Mo. Nanoparticles of these catalysts have been obtained
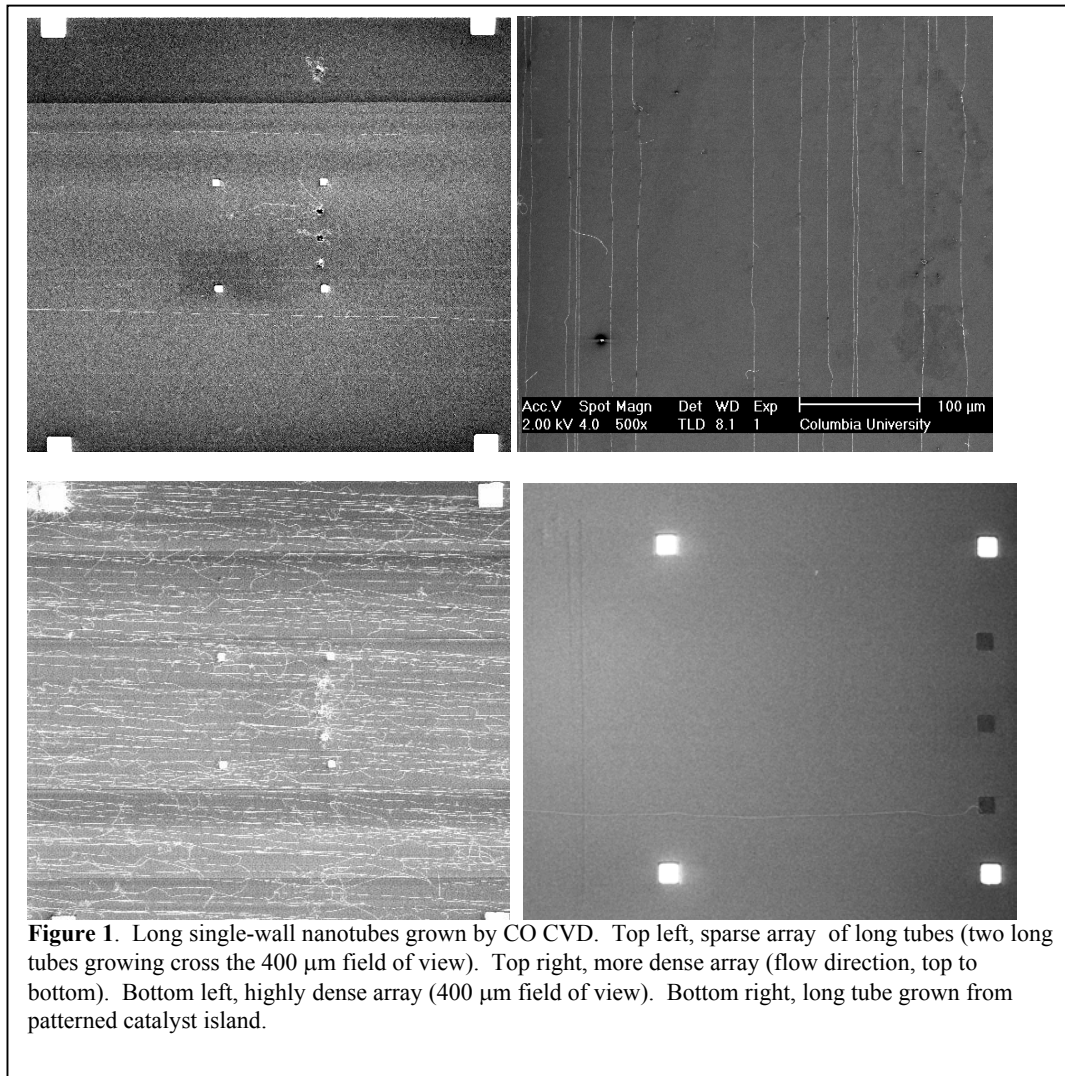
Figure 1. Long single-wall nanotubes grown by CO CVD. Top left, sparse array of long tubes (two long tubes growing cross the 400 μm field of view). Top right, more dense array (flow direction, top to bottom). Bottom left, highly dense array (400 μm field of view). Bottom right, long tube grown from patterned catalyst island.

by a number of methods, including chemical synthesis[19, 20], thermal treatment of thin films[21], precipitation of metal salts from solution[15], and use of iron-containing molecules such as ferritin[22].

CVD synthesis has many advantages over other methods for the fabrication of nanotube devices. CVD-grown nanotubes can be much longer and cleaner than bulk-grown nanotubes that are deposited from solution, and can be grown from patterned catalyst islands. It is possible to control the nanotube diameter by controlling the nanoparticle size. Recent work has shown that it is possible to control the direction of nanotube growth in CVD by the application of high electric fields[23] and the flow of feedstock gas[24-26].

A few groups have recently shown that ultra-long (up to the cm range) SWNTs can be produced by CVD[24,25,27]. Such tubes, either individually or in parallel arrays, are interesting for a both applications and basic science. Long SWNTs can be used to study basic transport properties[16] of nanotubes in the regime where the contacts are unimportant, and to examine the scaling of transport properties with length. In addition, thin films of long nanotubes should have lower resistivity than films of short tubes with equal density. Therefore, films of long nanotubes will exhibit higher performance, for instance as transparent, flexible electrodes for optical devices[29].

2.1. CO CVD

Carbon monoxide is a highly efficient feedstock for SWNT growth, both for bulk synthesis[17] and for direct CVD growth onto substrates. For direct growth onto substrates, CO is mixed with H_2 to optimize nanotube growth and minimize the

deposition of amorphous carbon. A significant advantage of CO as a feedstock is that the process window for SWNT growth is very wide: good growth is generally achieved for hydrogen concentrations of ~20% to ~70% at 900 °C.[16]

Another recent advance in nanotube CVD has been the efficient production of long SWNTs by a fast heating technique[24]. In this method, a substrate with catalyst is inserted directly into the hot zone of a furnace under flow of feedstock gas. Under these conditions, a significant proportion of SWNTs seem to grow by a 'tip growth' mechanism, where the catalyst particle is lifted off the surface[25]. This allows for very fast nanotube growth and alignment of the tubes with the gas flow in the CVD reactor.

We have used the fast-heating technique combined with CO feedstock to produce arrays of long, aligned SWNTs. Iron nanoparticle catalysts (diameter ~ 2 nm) are deposited on Si/SiO$_2$ substrates, either randomly or in patterned areas. The substrates are then inserted into a 1" diameter quartz tube that fits into a tube furnace (18" hot zone). The quartz tube is long enough (48") so that the sample can be moved in and out of the hot zone by simply sliding the tube. The substrates are first placed in the hot zone of the furnace and kept in pure oxygen at 650 °C for 30 minutes to burn off the organic capping layers on the nanoparticles and any residual photoresist on the substrate. The substrate is then removed from the hot zone. The oxygen flow is turned off and replaced (after an argon purge) with CO/H$_2$ at flow rates of 1000 SCCM for both gases. The oven is heated to 900 °C, allowed to stabilize, and the sample is quickly inserted into the hot zone. The substrate is maintained at the growth temperature for 20-30 minutes, followed by slow cooling in pure H$_2$ to room temperature.

Figure 1 shows arrays of long SWNTs that can be achieved by fast-heating CO CVD. The top left image shows a very sparse array of long aligned nanotubes: only two are visible crossing the 400 μm field of view from right to left (parallel to the CVD gas flow). The top right image shows an array with higher density (approximately 25 μm average spacing). It is interesting to observe that in this image, there are two instances of tubes that have grown very close to one another (< 5 μm spacing) without sticking together to

Figure 2. Long nanotubes synthesized by Ethanol CVD

form a bundle, even over very large distances. The bottom left image shows a highly dense array of long aligned tubes (<5 μm average tube spacing) over a 400-micron field of view.

It is also possible to grow long nanotubes from individually patterned catalyst pads, as shown in the bottom right image in figure 1. The pads were defined by photolithography employing a two-layer resist consisting of a layer of SU-8 photoresist on top of PMMA. Because PMMA is soluble in SU-8 developer, patterning the top SU-8 layer also selectively removes the underlying PMMA. After deposition of catalyst, the bilayer is lifted off in acetone. The PMMA acts as a release layer, while the SU-8 prevents stray redeposition of the catalyst onto the substrate.

2.2. Ethanol CVD

Figure 2 shows long aligned nanotubes grown by ethanol CVD. In this method, Co/Mo catalyst particles are encased in a mesoporous silica support that helps to prevent catalyst aggregation[30]. The silica/catalyst mixture is obtained by a
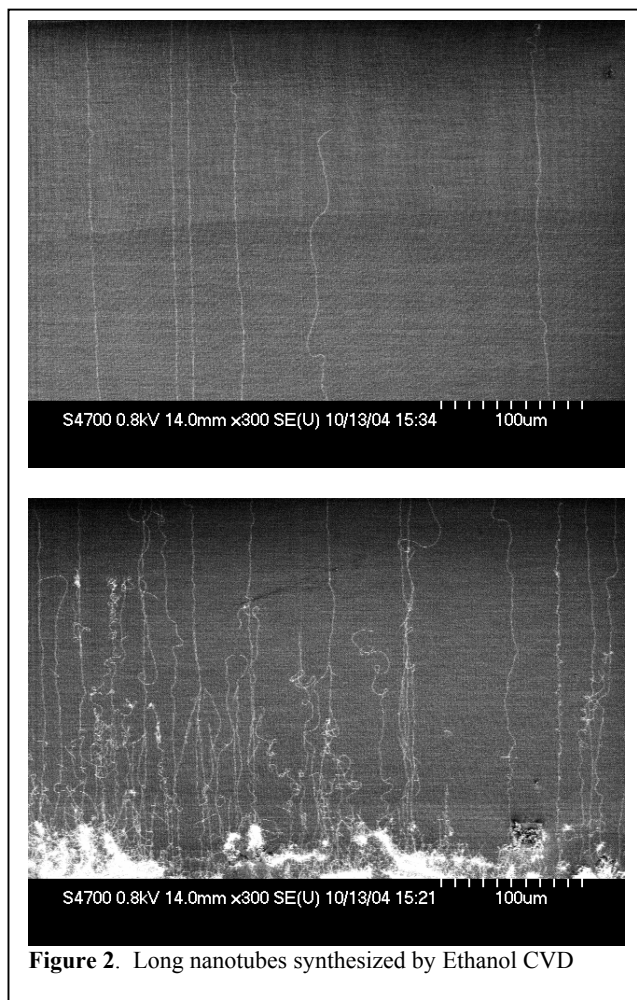
sol-gel method, so that thin films can easily be applied by spin coating, dip coating, or stamping. Ultralong aligned tubes are obtained by stamping the catalyst mixture on the upstream side of a chip. The catalyst is calcined in air at 550 °C; nanotubes are grown in a 1" quartz tube at 850 °C in argon (500 sccm) that is bubbled through ethanol (at 0 °C). Because of the high reactivity of the ethanol and the high activity of the mesoporous silica, nanotubes grow at a high rate (reaching mm lengths in 30 min.). It is likely that this high rate is crucial to obtaining, aligned nanotubes.

2.3. Freely Suspended Nanotubes

Using both the fast-heating CO CVD technique and the ethanol CVD technique, it is possible to grow freely suspended nanotubes over large distances. Figure 3 shows two SEM images of freely suspended tubes grown over ~100 μm slits in Si wafers. The slits are fabricated by anisotropic KOH etching of Si using a Si_3N_4 mask. Catalyst is placed on one side of the slit, and the chip is placed in the CVD reactor with the slit perpendicular to the gas flow so that long tubes are carried downstream over the slit. The left image in figure 4 shows nanotubes growing from the bottom of the image to the top, with the slit visible as the black region. The right image in figure 3 shows one of the nanotubes crossing the slit. Freely suspended nanotubes are useful for a number of investigations. We have recently used these samples to measure both the Rayleigh and Raman scattering spectra of individual SWNTs[31]. It should be possible to combine these techniques with electrical, mechanical, and TEM measurements to offer complete characterization of single tubes under various conditions.
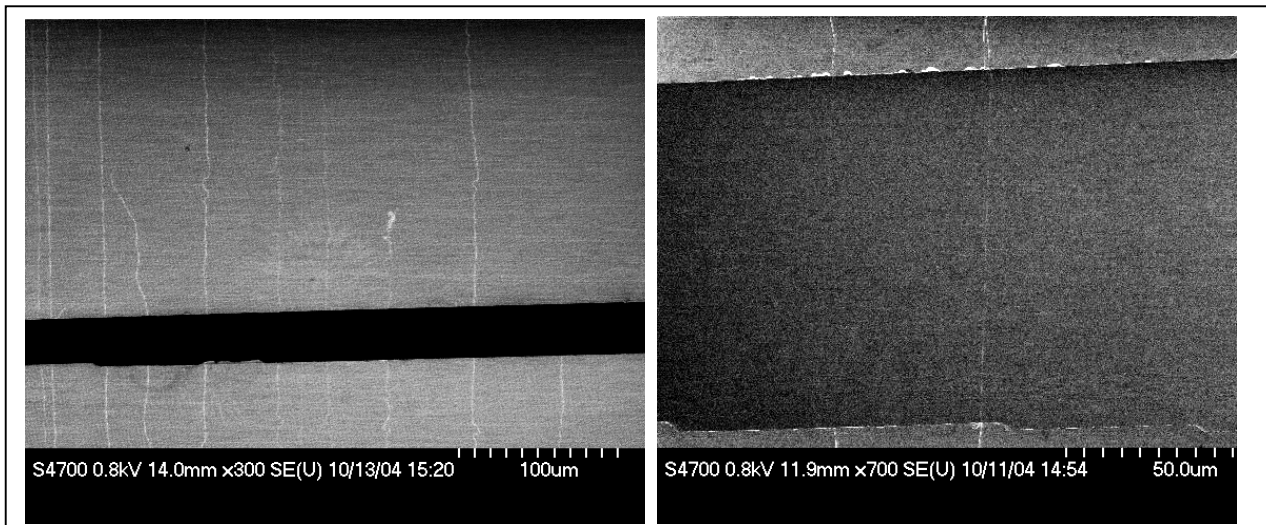

Figure 3. Freely suspended SWNTs grown over a slit etched into a Si wafer.

3. NANOTUBE ARRAY DEVICES

Long nanotubes and nanotube arrays can be used to fabricate a number of devices. Figure 4 shows a single long nanotube contacted by multiple electrodes, with spacings ranging from 200 nm to 40 μm, fabricated by electron beam lithography. These structures can be used to examine the length-dependence of the conductance of nanotubes, as well as to examine whether the electrical properties of individual nanotubes remain constant over their entire length.

Figure 5 shows a nanotube array device. Interdigitated finger pads (Cr/Au, patterned using e-beam lithography) contact a number of nanotubes in parallel in order to
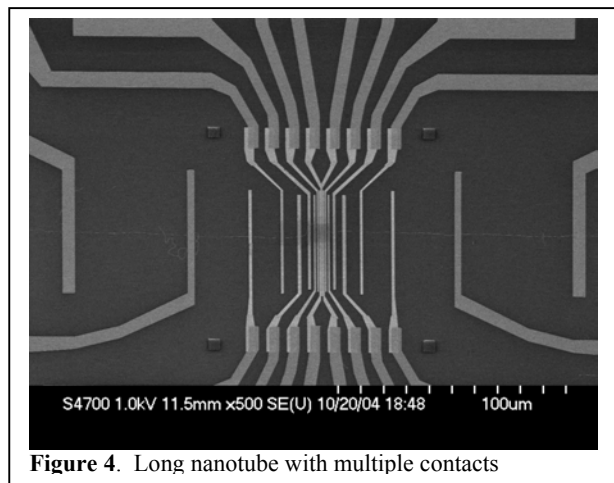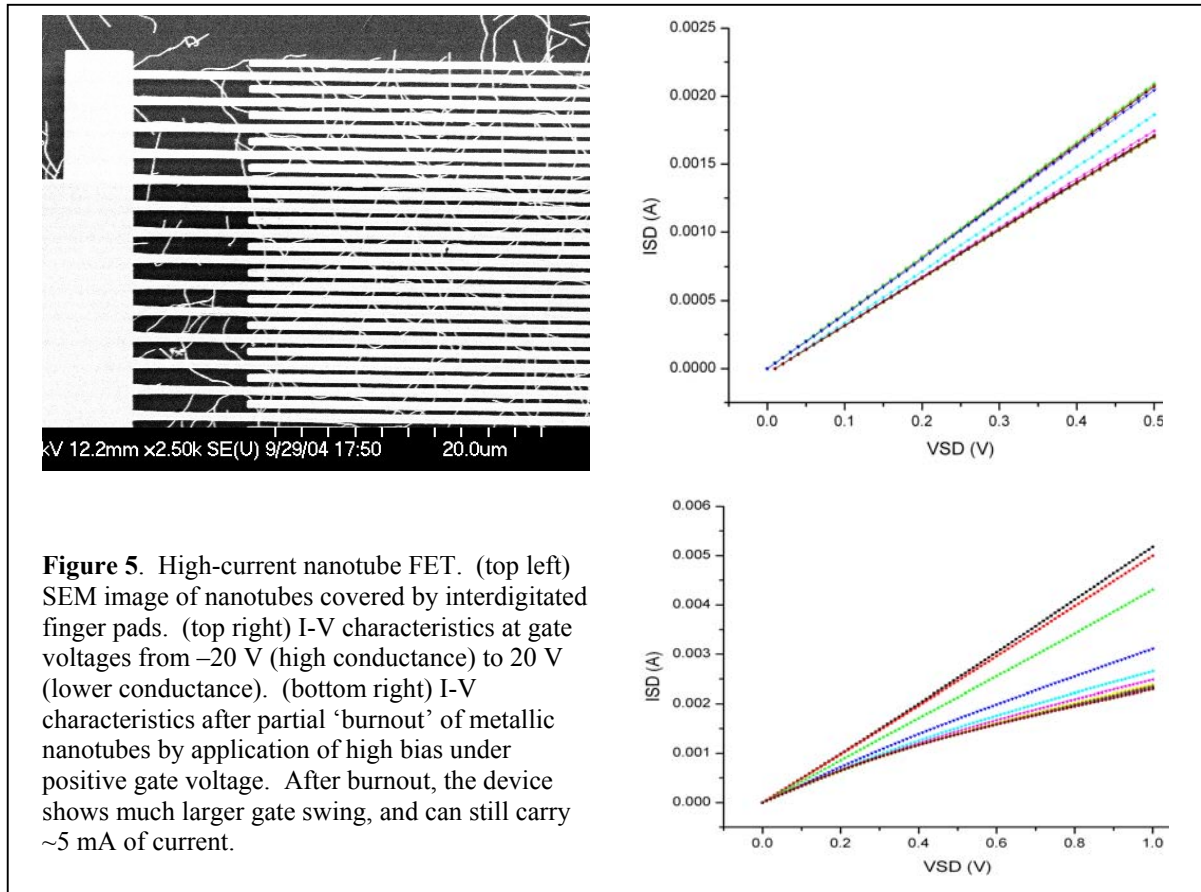

Figure 4. Long nanotube with multiple contacts

realize a low impedance device. The finger pads are positioned randomly on a substrate with a nanotube film (in this case, non-aligned); tubes extraneous to the devices are later burned away by oxygen plasma after a second e-beam lithography step to protect the tubes inside the device. Because it contains many tubes in parallel, this device can carry large currents. As grown (top right), the device shows a high conductance and a relatively small gate response due to a large number of metallic tubes shorting out the semiconducting ones. By applying a large positive gate voltage to turn off the semiconducting nanotubes and applying a large bias to the device, the metallic tubes can be selectively burned out. The bottom-right image in figure 5 shows the result of this treatment: the conductivity remains high, but the gate response is greatly increased. Such devices should be very useful for testing the high frequency properties of nanotubes, and as high-power transistors.

Figure 5. High-current nanotube FET. (top left) SEM image of nanotubes covered by interdigitated finger pads. (top right) I-V characteristics at gate voltages from –20 V (high conductance) to 20 V (lower conductance). (bottom right) I-V characteristics after partial 'burnout' of metallic nanotubes by application of high bias under positive gate voltage. After burnout, the device shows much larger gate swing, and can still carry ~5 mA of current.

4. Nanotube Field Effect Transistor Sensor

Chemical sensors 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 is very convenient. Indeed a number of researchers have reported that nanotube transistors are responsive to several gaseous agents[2-7]. In particular, Dai and his coworkers 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[3-7]. 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. In this section, we will discuss the possible principle of Nanotube FET sensors and their application to sensing alcoholic vapor and aqueous environment.

4.1 Principle of Nanotube FET Sensor

Electronic transport characteristic of SWNTs are sensitive to surface charge transfer and changes in the surrounding electrostatic environment[32-36]. Upon exposure to gaseous and aqueous molecules, the electrical resistance of field effect transistor (FET) made of an individual semiconducitng SWNT is found to dramatically increase or decrease. Initially it was speculated that such drastic change of the electric transport characteristics in SWNTs FET was due to adsorption of certain molecules or polymers, which dope the SWNTs and change the carrier concentrations[7,37]. SWNT FET, therefore, has been suggested as a chemical sensor for detecting molecules in the gas phase and biosensors for probing biological processes in solution.
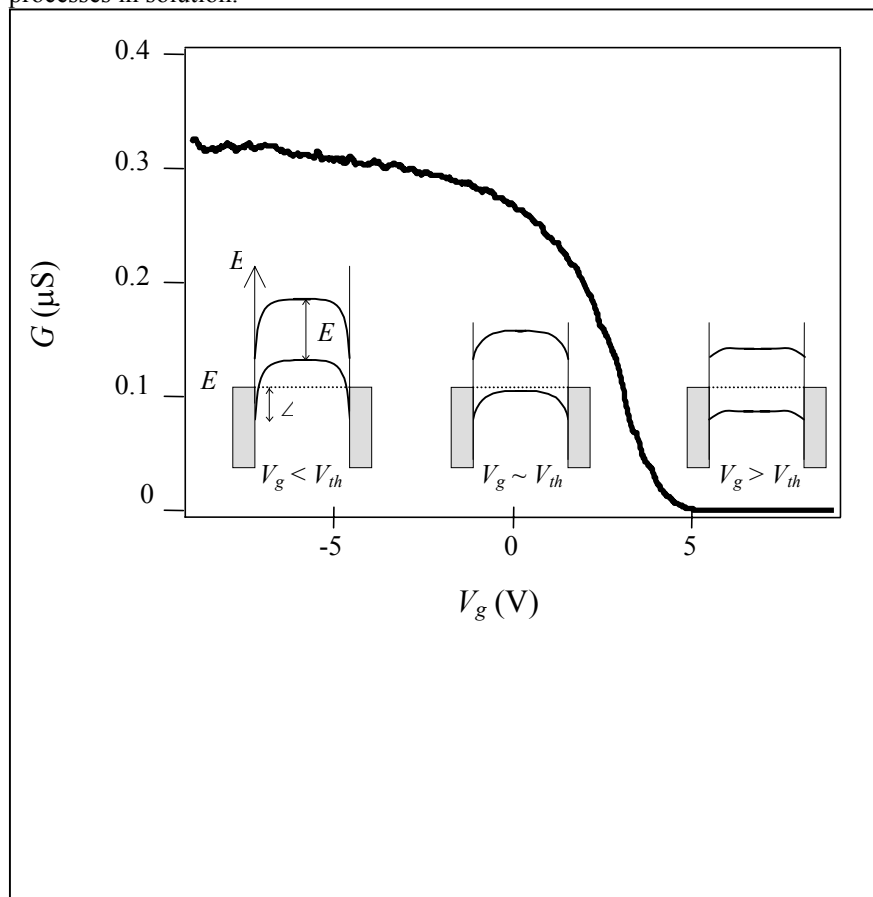
Despites of the initial promising demonstration of SWNT FET for chemical and even biological sensors, the major obstacle for SWNT FET sensory application is the lack of understanding of the exact sensing mechanism of the device. Specifically, recent experimental observations have suggested that often the intrinsic SWNT properties do not limit the electric characteristics of SWNT FET device. Instead, the existence of Schottky barrier at the SWNT/metal contact interface and their response to the applied electric fields at the gate electrode largely determine the electrical performance of FETs[38,39]. The development of these barriers is a consequence of the difficulty to create an ideal Ohmic contact. Figure 6 shows a typical SWNT FET device characteristic as the gate voltage V_g changes. A band diagram model based on Schottky barrier explains well the observed change of low bias conductance curves. Clearly, bulk doping- Schottky barrier issues are needed to understand for sensor application in future study in more controlled device geometry.

In addition, the adhesion of chemical substances on the substrate near the SWNT FET may change the local charge environment, which affects the device performances. 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. This substrate related effects also could alter the Schottky barrier at the nanotube-metal interface. 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.

4.2 CNT FET sensor for Alcoholic vapors

In our recent studies shown in Figure 7, it has been found that simple exposure of SWNT FET to even mild solvent such as ethanol completely changed the device characteristics. For these studies were using a device that has the metal/CNT junction uncovered to see how it responds to analytes. Both a significant shift of threshold voltage as well as strong

suppression of gate saturation current has been observed, which suggests that alcohol acts as a dopant and in fact transfers charge to the SWNT. However the same effects might be expected from the change of SWNT-metal junctions which will in turn changes the Schottky junction barrier properties as discussed above.

Although these preliminary observations do not provide a definite answer for this issue such as detailed interaction of chemical species to the SWNT and its junction, it is very interesting that we found there is a noticeable dependence in the FET performance on the partial pressure of applied analyte. Fig. 7(b) shows that when the partial pressure was changed from 60 to 30 mmHg, the slope of the current decay becomes smaller, but saturated to the exactly same value. Further decreasing pressure, however, the decaying rate becomes much less, and the current change does not saturate within the experimental time scale. This observation strongly indicates the slow dynamics of adsorption to either SWNT sidewall or SWNT-metal junction is responsible for the induced change as the analyte gas was introduced.
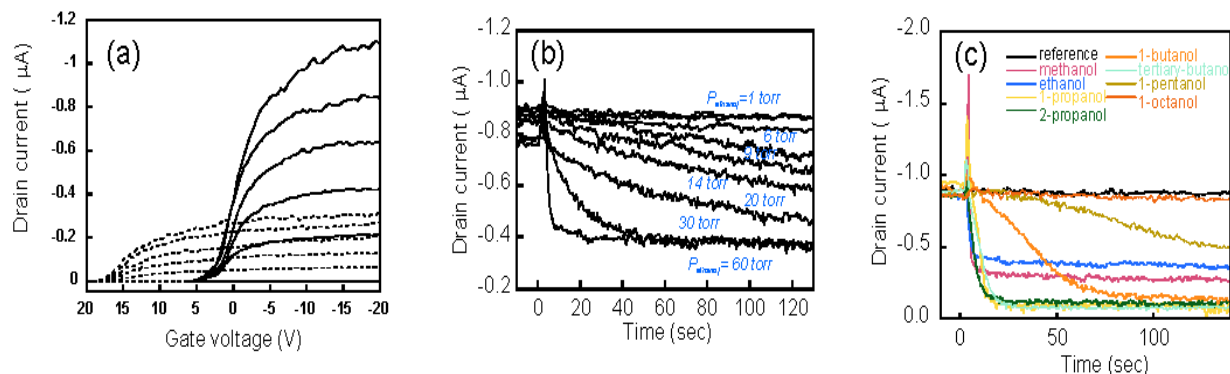

Figure 7. (a) nanotube FET characteristics measured with (broken line) and without (solid line) application of a saturated vapor of ethanol. (b) Partial pressure dependence of the source drain current I_{sd} of nanotube FET. (c) Single nanotube FET response to different alcohols (adopted from ref [39]).

In addition, we have found that these SWNT FETs are also responsive to alcohol vapors of varying chemical composition. Figure 7(c) 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 started at t=0 sec. Response to methanol, ethanol, 1-propanol, 2-propanol, and tertiary-butanol is rapid and current reduction saturates within 5-15 sec. 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. 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.

4.3 Junction Protected CNT FET Sensors

The PIs intend to focus on SWNT sensing mechanism in the initial phase of this project. Carefully designed FET structure which protect the junction areas from electrical degradation due adsorption of analytes are essential to separate the junction related sensing mechanism and the tube related mechanism.

In addition to understanding the sensing mechanism mentioned above, maintaining device stability in various different environments is required for SWNT FET sensor applications. It have been reported that SWNT FET that come in contact with water or oxygen can cause irreversible degradation of device performance[6,38]. For practical sensor application, however, it is important that the device maintains predictable reversibility, reproducibility, and sensitivity to various analytes. Especially for most of detecting of biological substances, *in vivo* biochemical sensing in aqueous condition is essential.

The problem of stability of the devices in hostile environments can however, be solved by simply capping the inactive part of channel with insulating and non-permeable film. The PMMAS and thin silicon oxide layers have been tested for capping materials for SWNT FET. Especially, PMMA has been widely used for its readiness for creating fine lithographic patterns and for its effectiveness to provide protection against doping of alkali metals, such as

potassium[32,33]. Although PMMA is effective in this application it failed with numerous gases and solvents due to its permeability.
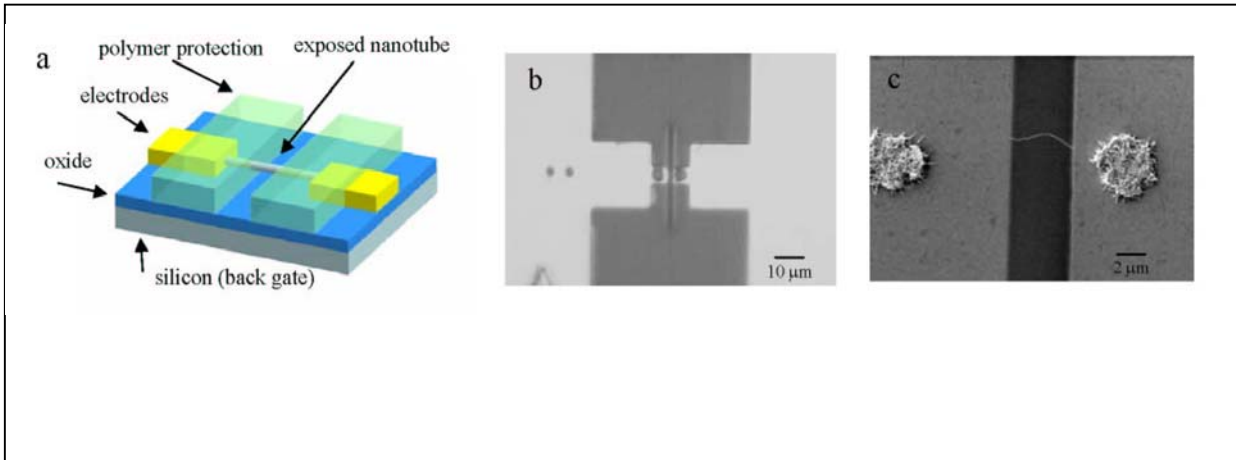
We have fabricated SWNT FETs incorporating an electrode protection scheme and demonstrated very reproducible and reliable measurement in aqueous environment (Fig. 8). SWNTs are synthesized by chemical vapor deposition (CVD) on patterned substrates and electrodes are defined using optical lithography or electron beam lithography. We found that if the SWNT FETs did not have the contacts covered water-mediated degradation of device performance occurs primarily near the contact regions (*vide infra*). This degradation of device performance can be avoided by coating the source and drain electrodes with a hydrophobic photo expoxy such as SU8. It is known that a cross-linked SU8 epoxy layer is chemically inert and able to form a very tight non-permeable coating on a silicon surface.
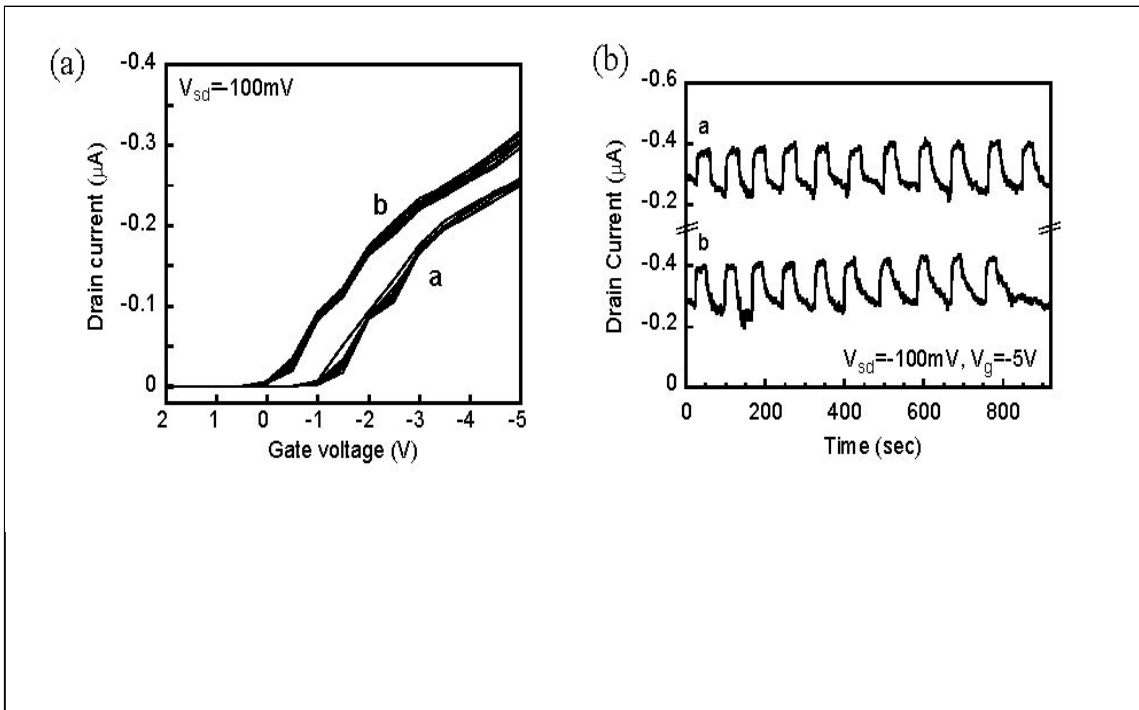
Figure 9 shows the results that demonstrate stable measurements are possible even under the conditions where the active channel is exposed to water. The gate voltage dependence of drain current is measured under water looks very similar to those without water although the threshold voltage is changed by about 1 Volt. This response has been proven to be reversible and very reproducible as shown in Figure 9(b). More than hundreds times the measurement could be reproduced without noticeable device performance degradation.

This data suggests that our scheme of using a junction protected device clearly removes an ambiguity for current limiting cause of SWNT FET device, and allows us focus only on the change of bulk portion of SWNT in the device. Since the adsorption control of gas or aqueous solution to the SWNT and metal junctions are extremely difficult, our strategy to separate out the junction phenomena in electron transport in SWNT FET from the bulk effects in different environments will be extremely useful information to understand the sensing mechanism of these devices.

5. Nanotubes for Nanoscale Electrode

The method we discussed so far is electrical sensing using the analysis of FET characteristics. Such characteristics include the gate threshold voltage, subthreshold slope, gate saturation currents, and source drain saturation current. In principle, these characteristics can be deduced from the mobility of charge carrier and the barrier height with given geometry for electrostatic coupling with gates. However, largely uncontrolled nature of SWNT contacts prevents such simple analysis for most of case. The combination of highly localized selective covalent functionalization (shown below) of the SWNT side wall and extremely sensitive thermoelectric detection could allow us to detect stochastic single molecular binding events, which is the ultimate goal of molecular sensing. Using state-of-art electron lithography, it is possible to expose only ~5 nm channel length of SWNT FET. *In situ* oxidation on this exposed section of the SWNT may provide only a small number of reaction sites which can be used to monitor a stochastic process of single molecular binding. In this section, we briefly discuss our on-going project to create small

5.1 Local Oxidation of SWNT Sidewall by Electron Beam Lithography

First the SWNT two terminal devices were fabricated by the standard method described above. In order to create very narrow exposed region of SWNT for oxidation, we employed the second stage high resolution electron beam lithography. A 50 nm thick PMMA single layer is used for a resist layer for lithography by spin-casting PMMA/MIBK dilution. 30K volt of acceleration voltage was used to write ~5 nm normal line width on this single layer resist followed by developing the exposed resist in water and isopropan alcohole mixture at low temperature (4 C). With this method, we typically remove the expolsed resist part very selectively, resulting the gap opening 5-10 nm. After developing, we use an reactive ion etching using oxygen plasma to oxidize the exposed part of tube selectively. Most of exposed part of SWNTs are completely oxidized by exposing in the oxygen plasma for long time. By adjusting the exposing time to the plasma, we can control the degree of the demage of the SWNT sidewall.

Figure 10 shows an atomic force microscope image of a SWNT with completely oxidized section. The inset shows the exposed section of the SWNT is completely removed by oxgen plasma etching. Due to the tip convolution effect, however, it is difficult to obtain the exact morpology of the oxidized section of the SWNT. The deive was found that electrically disconnected after
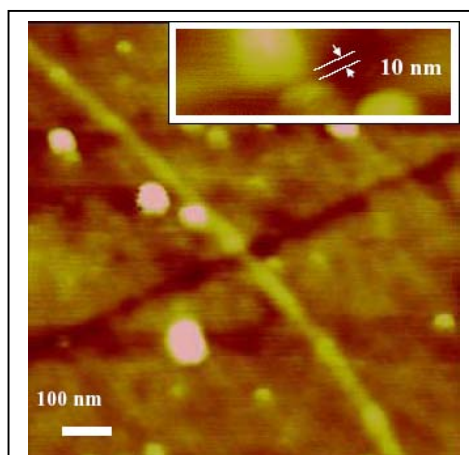

Figure 10. Atomic force microscope image of SWNT with completely oxidized section by selective exposure to reactive ionic oxygen. The inset shows the zoomed in image of the gap region.

the plasma etching as we expected. We found that the degree of oxidation can be controlled by choosing different plasma density as well as adjusting the exposure time. Electrical conduction measurement often can be used for testing the degree of oxidation. The SWNTs with a completely oxidized section do not carriers current, while partially oxidized SWNTs exhibit an order of magnitude decreased conductions compared to the orignial conductance before the oxidation process.

5.3 Chemical Snesitivity of Demaged CNT sidewall

The selective local oxidation of SWNTs described in the previous section can be used to fabricate a SWNT sensor. The partially oxidized sidewalls of SWNTs can serve as localized reaction sites for molecular bonding from the environment. Specifically, functionalization on this exposed section of SWNT will provide only a small number of covalent binding sites which can be used to monitor a stochastic process of single molecular binding. As an initial step, we exposed the SWNT devices with a partial local-oxidization section to a solvent such as iso-propan alcohole (IPA). Figure 11 shows the conductance change of a SWNT device with partial oxidation upon exposure to IPA. This device had two-terminal conductance ~ 15 μS before it was oxidized and the value drop to ~ 7 μS after the oxidation step. It was found that the device shows a very sensitive reaction upon exposure to IPA injection, which was completely absent prior to the partial local-oxidation described in the previous section. The conductance drops sharply (<0.1 sec.) when the oxidized section is exposed to IPA and then it recovers quickly upon the removal of the IPA exposure (~ 1 sec.). Such sensitivity is an order of magnitude better than that of the sensors demonstrated in the section 4 which employs the SWNT FET, detecting electrostatic environment change.

Figure 11. Source drain conductance change in the SWNT nanotube device with partial oxidation of small section of sidewall upon exposing to iso-propan alcohole

This experiment is now being test out multiple batch devices fabricated by the method described in section 2 in order to obtain statistical data in different device geometry, preparation method using different chemical analytes.
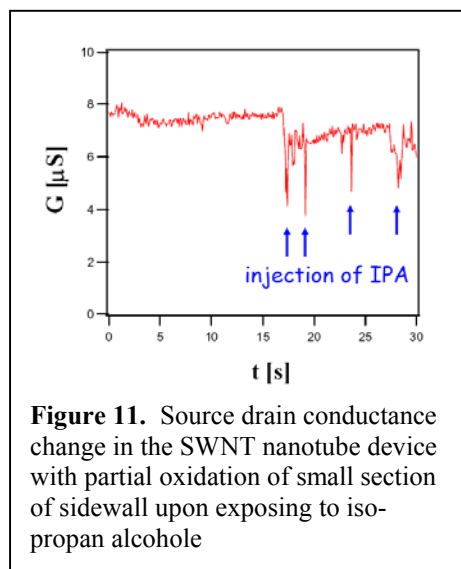
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