SUNFEST Technical Report TR-CST01NOV04, Center for Sensor Technologies, Univ. of Pennsylvania, Philadelphia, PA, 2004

University of Pennsylvania
Center for Sensor Technologies

SUNFEST

NSF REU Program
Summer 2004

INTEGRATED ELECTROCHEMICAL GATING OF CARBON NANOTUBE FETs FOR BIOSENSING APPLICATIONS

NSF Summer Undergraduate Fellowship in Sensor Technologies
Emmanuel U. Onyegam, Electrical Engineering
University of Texas at Dallas

Advisor: Dr. A.T. Charlie Johnson, Dept. of Physics and Astronomy
University of Pennsylvania

ABSTRACT

Carbon nanotubes have emerged as the leading candidate of electronic materials used for future nanoscale chemical and molecular sensors. Recently, nanotube field effect transistors (CNFETs) have been exploited as biodetectors of the thyroid hormone, triiodothyronine (T3). Although significant progress has been towards the development of actual nanotube based sensor devices, the next challenge is to integrate the devices into a single chip. Numerous gate configurations to CNFETs have been proposed, but few have been shown to be effective, and even fewer can be integrated to a chip. An electrolytic “tip” gate design has been shown to be more effective than the conventional backgate geometry. The drawback to the “tip” gate geometry lies in the fact that an external electrode is required to gate the devices. In this paper, a novel integrated gate design is proposed. Lithographically patterned electrodes on the chip surface are fabricated to effectively gate CNFET devices.

TABLE OF CONTENTS

1. INTRODUCTION

Carbon nanotubes (CNTs) are one-dimensional nanoscale structures with unique electrical, chemical, and mechanical properties. There are two kinds of CNTs: single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). Although MWNTs were discovered first (in 1991), SWNTs have been studied more because of their simpler and more stable physical structure. The structure of a SWNT is equivalent to a sheet of graphene rolled up to form a cylinder[1]. Depending on their chirality, SWNTs can exhibit either semiconducting or metallic characteristics; this is perhaps the most important reason scientists and engineers are interested in them. Field-effect transistors (FETs) based on semiconducting SWNT for example, have been found to have carrier mobilities and transconductances that far exceed that of silicon[2], the best known semiconducting material and the active element in modern electronic devices. On the other hand, metallic nanotubes have been shown to have conductivities that rival some of the finest metals such as copper.

With the semiconductor industry facing increasing challenges in scaling silicon devices to smaller dimensions, carbon nanotubes are certainly one of the most promising candidates for future nanoelectronics. The remarkable properties of nanotubes have led to their being exploited as channels in FETs, field emission display sources, scanning probes, and memory devices. Furthermore, because of their extreme sensitivity to chemicals on their surface, nanotube based chemical and molecular sensors have also been reported[1-3, 5-8]. While significant progress has been made towards the realization of nanotube based sensors, one of the challenges faced lies in the integration of the sensing components into single devices. Here, we present a novel integrated electrolyte gating of CNFETs.

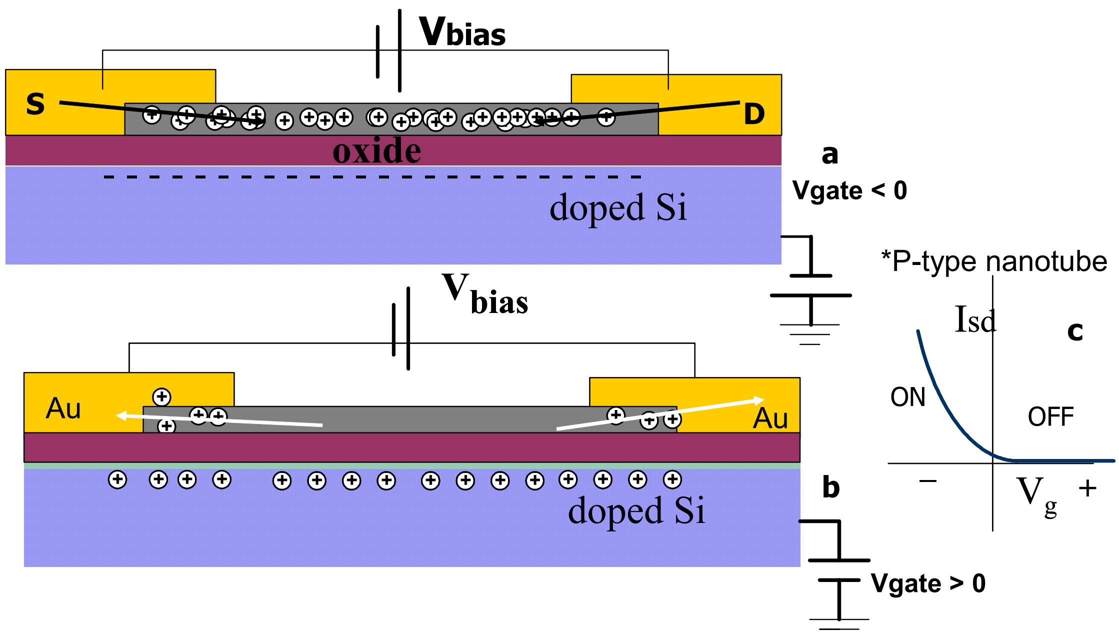

Figure 1. Schematic and I-V characteristics of a nanotube transistor. (a) For negative gate voltages the device turns ON due the accumulation of excess positive charge carriers. (b) Positive gate voltage result in the depletion of charge carriers into the metal contacts, thus turning OFF the device. (c) I-V curve showing the response of the device to positive and negative gate voltages

2. NANOTUBE FETS

Single walled nanotube transistors are electronic devices based on a semiconducting nanoscale molecule. Figure 1 shows the structure of a carbon nanotube transistor along with its I-V characteristics. Nanotube transistors consist of a semiconducting carbon nanotube typically 1 to 2 nm in diameter bridging a gap of about 1 um, formed by two closely separated metal electrodes which are fabricated on a Si substrate. The source-drain electrodes are usually patterned via electron-beam (e-beam) lithography. Gold electrodes commonly serve as the source-drain leads. Applying a voltage to the silicon substrate turns on and off the flow of current across the nanotube-channel by controlling the movement of charge carriers onto it. A bias voltage applied to the source-drain electrodes is used to establish the direction of current flow along the tube.

At zero at gate voltage, there is little current flow across the nanotube. The source of the charge carriers is not clear; the carriers may be intrinsic to the nanotube (due to doping) or could come the source-drain electrodes due to work function differences. Application of negative gate voltage results in the accumulation of positive charged holes (from the electrodes) across the nanotube, which are then free to conduct current (figure 1a). The characteristic of a CNFET is very similar to that of a Si-channeled MOSFET. As shown in the device I-V characteristics of figure 1c, the current across the nanotube increases strongly with a more negative gate voltage, and decreases for positive voltages.

This is a typical behavior of a p-type semiconducting SWNT, one with holes as majority carriers. Typically, nanotubes are grown to be p-type; research suggests that this results from oxygen doping[3] during growth. There have been reports of n-type characteristics achieved via alkali metal n-dopants such as potassium or by polymer doping[3]. Furthermore, some devices exhibit both p-type and n-type behavior, referred to as ambipolar. Ambipolar characteristics are generally due to the Schottky barriers at the metal-nanotube interface.

The interest in nanotube-FETs lies in their potential to perform better than conventional silicon based FETs. Parameters such as *mobility* and *transconductance* dictate the performance of a FET. Mobility is a measure of the ease with which electrons and holes can flow through a material[4]. Hole mobilities in the range of 2,000 to 4000 cm^2/V-s for CNFETs have been reported[5] compared with 500 cm^2/V-s for Si MOSFETS. Furthermore, CNFETs have also been shown to have significantly higher transconductance, the measure of current carrying capability of FETs. High transconductance implies that the transistors can operate faster. Along with their small size and versatility as chemical and molecular sensors, nanotubes certainly have several advantages over silicon for future nanoelectronics.

3. NANOTUBE SENSORS

The electrical resistances of semiconducting SWNTs change dramatically when exposed to chemicals. This property makes them useful for chemical and molecular sensing. Sensing is achieved by exposing nanotube-FET devices to chemicals and monitoring the change in conductance. Nanotube based detection of various gases and chemicals has been reported by several groups. J. Kong et al reported[6] the detection of gases such as NH_3 and NO_2, while the detection of protein-receptor interactions such as streptavidin-biotin binding[7] was reported by A. Star et al.

The possible electrical interaction between DNA and the thyroid hormone, triiodothyronine (T3), is of interest to chemists and biologists. T3 is formed by two

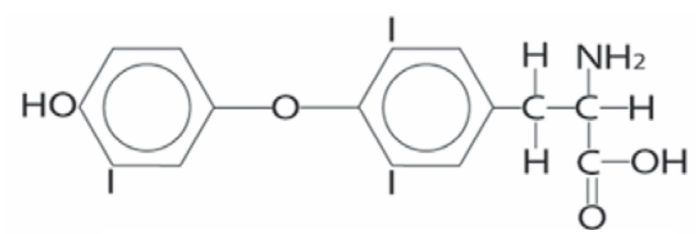

Figure 2. Structure of the T3 molecule

benzene rings decorated with three iodine atoms, as shown in figure 2. The role of the iodine atoms is not well understood. One theory is that iodine is essential to the *electrostatic* interaction between T3 and DNA[1]. Because the electronic properties of DNA are not well understood, carbon nanotubes provide a possible model for DNA as 1-dimensional conductors[1], assisting in understanding the electronic properties of T3.

Figure 3 shows the I-V_g characteristics of a CNFET device before and after exposure to T3. Before exposure to T3 (black curve), the device was characterized by placing a drop of a NaOH solvent on the device and taking ±0.8V electrolyte gate sweeps (refer to *Section 4*, "Gating Techniques"). Afterwards, the devices were exposed to a 0.1mM T3 solution dissolved with 0.1 mM NaOH in water; further gate sweeps were taken at a constant bias voltage of 10mV. As shown in figure 3, the device exhibits a shift in conductance towards negative gate voltages in response to the presence of T3. The device characteristics suggest that nanotube is p-type. Electron donation from T3 effectively shifts the valence band of the nanotube away from the Fermi level, which results in hole depletion, thus the left shift in conductance. Experimentation suggests that the amount of shift strongly depends on the concentration of T3, with stronger shifts at higher concentrations due to greater T3-nanotube charge transfer. Biodetection of T3 is achieved even at concentrations as little as 1uM.

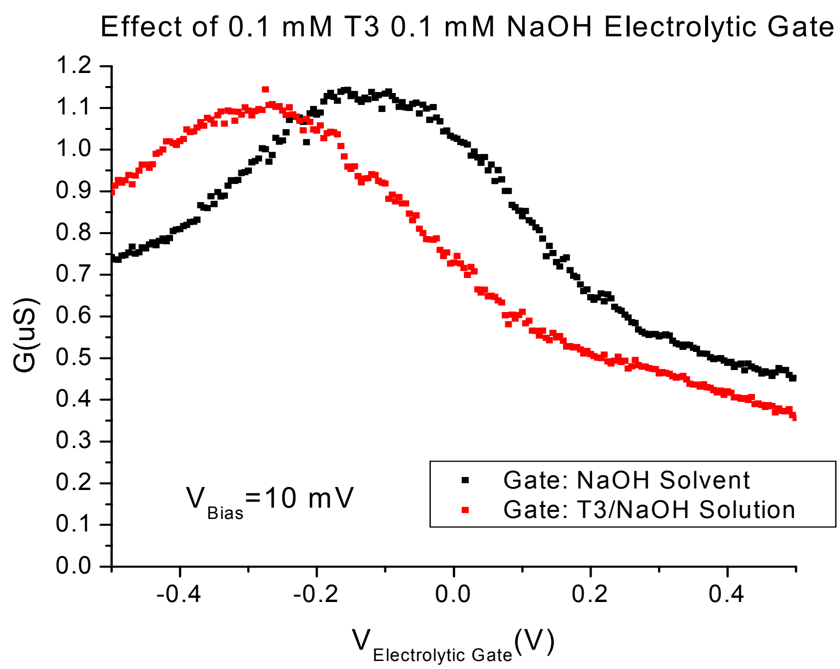

Figure 3. Shift in conductance vs. gate voltage after exposure to T3. The black curve represents the initial device characteristics prior to T3 exposure. The device characteristics after exposure to T3 is shown in red.

4. GATING TECHNIQUES

The mechanism of gating nanotube FETs for biosensing is of interest for optimal device performance. The most widely used gating techniques are the *backgate* (or *bottom-gate*) and *tip-electrolytic gate*. The *backgate* is the most common and oldest method of gating FET devices. In this configuration, devices are gated by applying voltage to the supporting silicon (Si) substrate (Figure 4a). An oxide material usually more than 100 nm thick serves as the gate dielectric. One disadvantage of the backgate geometry is that it requires all devices on the substrate to share one gate, so the devices cannot be addressed individually. Additionally, due to the thickness of the gate dielectric, the voltage required to turn on the devices is very high.

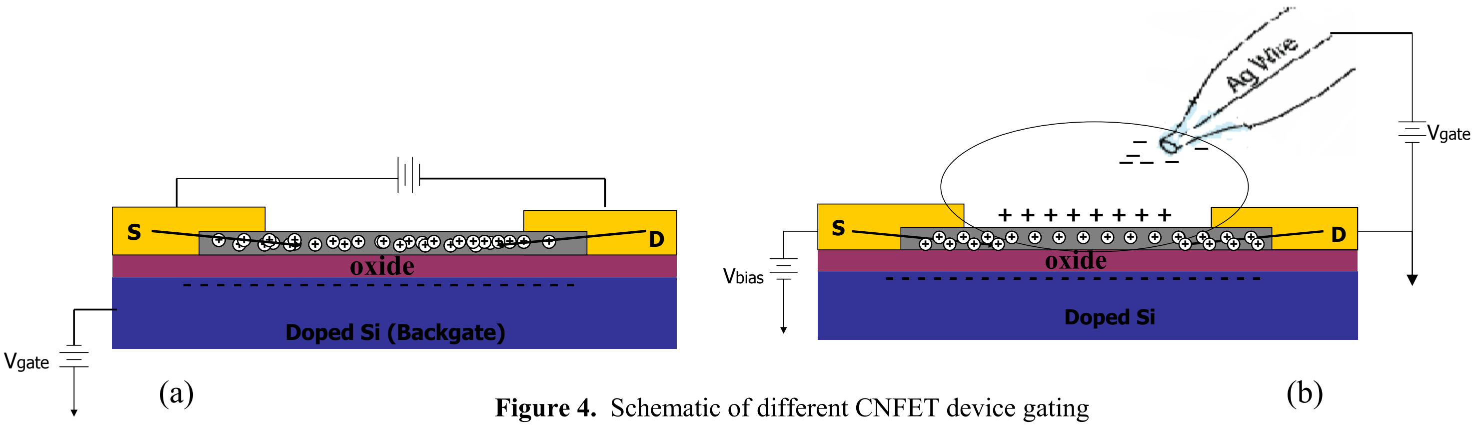

Figure 4. Schematic of different CNFET device gating geometries. (a) Backgate geometry. (b) Electrolyte "tip" gate geometry.

The tip-electrolyte gating technique (figure 4b) addresses these weaknesses. The idea is that by placing the gate as close as possible to the nanotube, ultimately into intimate contact, the device transconductance is dramatically increased[8]. The setup is similar to that described by Rosenblatt et al. A micropipette is used to place a micron-sized electrolyte droplet over the nanotube device. A voltage applied to a silver wire in the pipette is used to establish an electrochemical potential in the electrolyte relative to the device. The electrolyte functions as a well-insulated liquid gate and exhibits a strong capacitive coupling between the gate and the tube. As shown in Figure 5, the end result is a much lower operating voltage and steeper switching behavior. The drawback to the tip-gating regime however lies in the fact that an external electrode is used to gate the devices, making it difficult to integrate into chips.

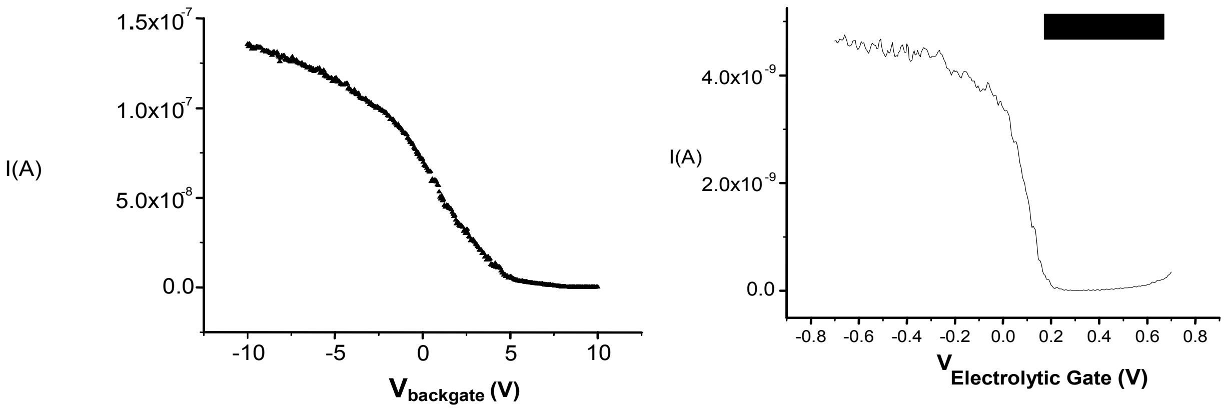

Figure 5. Response of a semiconducting SWNT to: **(**Left**)** Backgate configuration. **(**Right**)** Electrolyte "tip" gate configuration. V_{bias} = 10mV.

In this report, we present a novel integrated gate geometry. We exploit the strong gate coupling effect of the tip-electrolyte configuration and fabricate electrodes on the chip surface to gate the CNFET devices. According to our results, the new design effectively gates the CNFETs and its efficiency is comparable to the results achieved with the externally applied tip-gate setup. Figure 6 shows the structure of the proposed integrated gate CNFET.

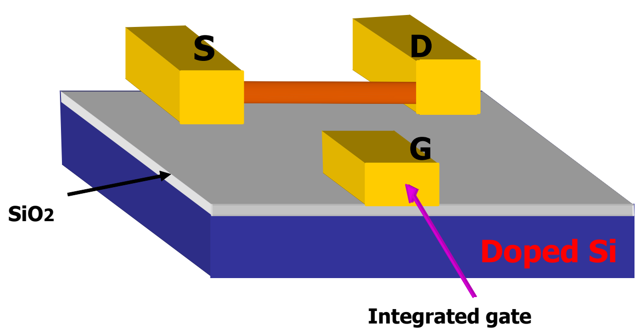

Figure 6. Schematic of an integrated gate CNFET

5. DEVICE FABRICATION

Our nanotubes were synthesized via chemical vapor deposition (CVD) following an approach similar to that described by Rojas et al. Fifteen drops of a 100 mg/L iron nitrate, $Fe(NO_3)_3 \cdot 9(H20)$, in isoproponal were spun onto a degenerately doped Si substrate layered with 400 nm of SiO_2. The substrates were then heated to 900ºC in an Ar atmosphere and growth was carried out for 15 minutes under 3500 sccm CH_4 and 450 sccm H_2. Subsequently, several hundred source, drain, and gate leads were randomly patterned on the substrate using electron beam (e-beam) lithography. The source-drain separation is approximately 1 µm, while the gate is positioned 10 µm from the center of the source-drain leads. Finally, 10 nm of Cr and 30 nm of Au were thermally evaporated onto the patterns. Chromium serves as an adhesive of gold to the SiO_2 substrate.

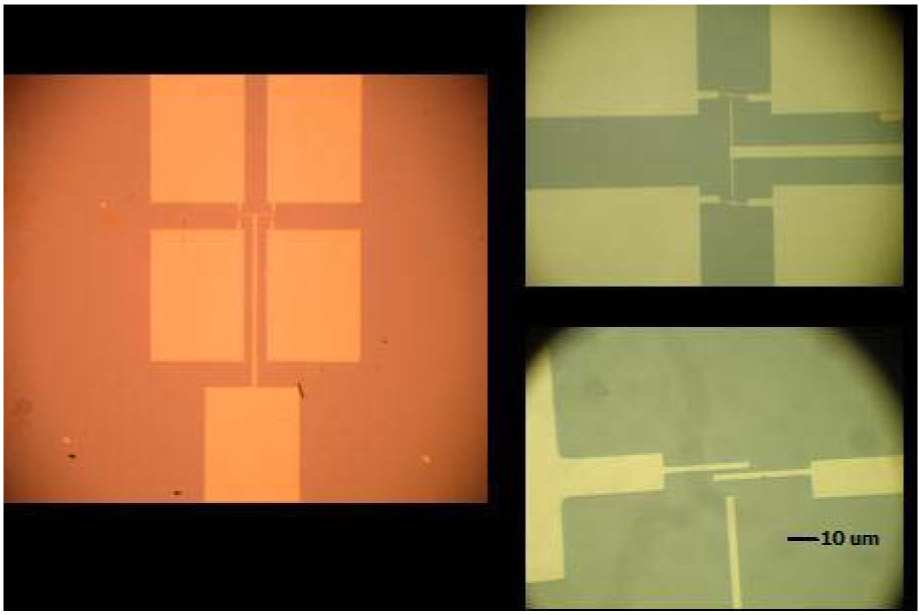

Figure 7. Optical images of an integrated gate configuration. Source-drain gap = 1 µm, gate distance = 10 µm from source-drain leads.

6. RESULTS AND DISCUSSION

Figure 7 shows photographs of the completed device structure. The devices were fabricated such that two pairs of samples shared a single gate to minimize the circuitry involved. Typically, we were able to attain 10-15 circuits with one s-SWNT for every 150 pairs of source-drain electrodes. Approximately 30 leads are bridged by metallic SWNTs while few leads are contacted by multiple or bundled SWNTs. Figure 8 shows the I-V_g curves for the two electrochemical gating methods, the previous external "tip" gate technique and the novel integrated gate geometry. A NaOH in DI-water solution was the electrolyte of choice. The new integrated electrode effectively gates our CNFETs, with the two methods exhibiting similar switching characteristics. The devices proved to be ambipolar, with strong conductance in either direction. Although a comparable gate response to the initial external gate configuration was achieved with the new integrated gate CNFET, there is a noticeable difference in the current drives. This is possibly due to the much thicker diameter Ag wire used for the external gate.

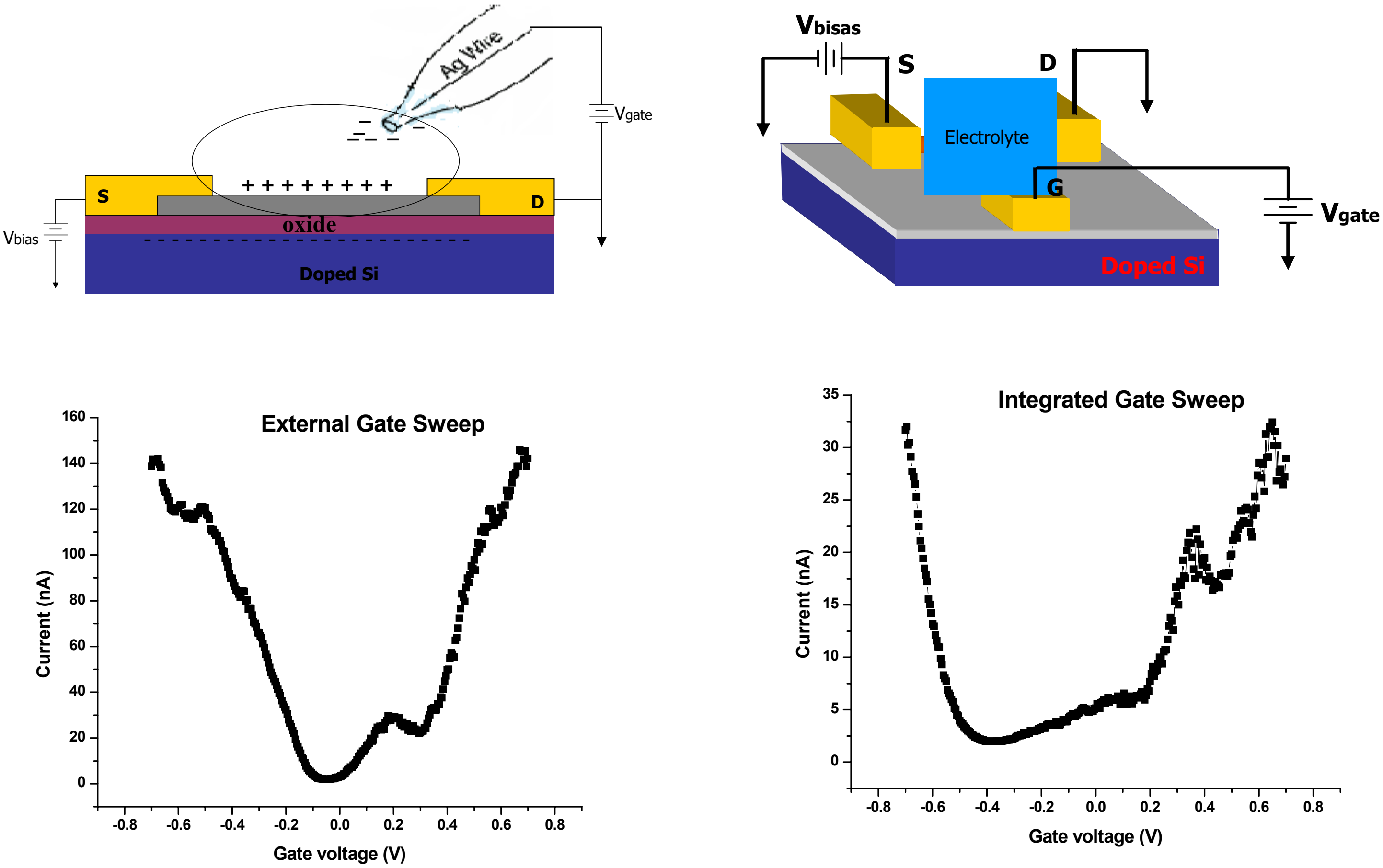

Figure 8. Response of a semiconducting SWNT to (Left) Backgate configuration (Right) Electrolyte "tip" gate configuration. V_{bias} = 10mV.

7. CONCLUSIONS AND RECOMMENDATIONS

The results presented show that the biodetection of the thyroid hormone, T3, is possible via electrochemical gated CNFETs. Electrochemical gating of CNFETs has been shown to have stronger gating effects than the conventional backgate geometry. However, the challenge of integrating device components into single chips has led to our fabrication of a novel device gating structure. Lithographically patterned on-chip gate electrodes are fabricated.

Our results show that the new integrated gate structure act as effective gates to CNFET devices. Comparison of the gate response of the new structure to the previous externally gated configuration proves that similar switching behaviors at low device operating voltages can be attained. Though it is not much of a concern, the current drive attained with the integrated gate is less than that for the external gate. One solution to this might be to increase the thickness of the integrated Au gate electrodes. Nevertheless, our new integrated gate structure offers advantages such as, individual addressability of devices, strong gate capacitive coupling and low device operating voltage.

Besides the advantage of integration offered by our new gate structure, a project proposal (not yet underway) is the design of a microfluidic array of channels whereby fluidic paths are fabricated to direct an automatic flow of electrolyte solution to various samples such that several devices can be tested simultaneously. This task would be almost impossible with the previous gating technique since multiple external gates would be required. The microfluidic arrangement will prove especially valuable to our current T3 experiments; instead of having to apply drops individually to the samples, a single drop will be applied which then can be directed to different samples. Hence, multiple devices can be tested at a fraction of the normal time.

8. ACKNOWLEGEMENTS

I would like to thank my advisor, Dr. A.T. Charlie Johnson from the Department of Physics and Astronomy, for his assistance, expertise, and kindness. I also would like to thank Mike Stern, Deirdre Smith, and everyone from Professor Johnson's Group for their contributions to this project. I am very grateful of this wonderful opportunity given to me by the SUNFEST program. Thanks to Dr. Van der Spiegel, the SUNFEST staff, and my fellow SUNFEST students for all the great memories. Thanks to my generous sister, "Chika" Onyegam for supplying me with food (a difficult task) and her patience. Finally, thanks to my professor, Dr. Lawrence Overzet from the University of Texas at Dallas for his inspirations. This research was funded by NSF through the SUNFEST REU program.

9. REFERENCES

[1] E. Rojas, Carbon nanotube-based biodetection of triiodothyranine, *SUNFEST Report 2003.*
[2] P.L. McEuen, J.Y. Park, Electron Transport in Single-Walled Carbon Nanotubes, *MRS Bulletin,* **April 2004**.
[3] H. Dai, Carbon Nanotubes: Synthesis, Integration, and Properties, *Accounts of Chemical Research,* **2002**, Vol. 35, NO. 12.
[4] B.G. Streetman, S. Banerjee, *Solid State Devices,* Upper Saddle River, NJ: Prentice Hall 2000
[5] S. Rosenblatt, Y. Yaish, J. Park, J. Gore, V. Sazonova, P.L. McEuen, High Performance Electrolyte Gated Carbon Nanotube Transistors, *Nano Letters,* **2002**, Vol. 2, No.8, 869-872.
[6] J. Kong, N.R. Franklin, C. Zhou, M.G. Chapline, S. Peng, K. Cho, H. Dai, Nanotube Molecular Wires as Chemical Sensors, *Science,* **Jan. 28, 2000,** Vol. 287.

[7] A. Star, J.P. Gabriel, K. Bradley, G. Gruner, Electronic detection of specific protein binding using nanotube FET devices, *Nano Lett., 2003, Vol. 3, No. 4.*
[8] M. Kruger, M.R. Buitelaar, T. Nussbaumer, C. Schonenberger, Electrochemical carbon nanotube field-effect transistor, *Appl. Phys. Lett.,* **2001,** Vol. 78, No.9.