The Role of Carbon Nanotubes in Sensing Applications

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Abstract

Four CNTFETs were fabricated with Cr/Au source and drain contacts and an Al top gate contact, using Al_2O_3 as a gate oxide dielectric which forms when Al is deposited on the carbon nanotubes (CNTs). The CNT devices were tested in both FET and two contact operation to determine their electrical characteristics. The devices were fabricated so that the change in capacitance between the gate and channel could be measured. However, the capacitance of the devices could not be measured because the oxide layer was too thin to effectively serve as a dielectric. When the I-V characteristics of the devices were tested using one Al contact and one Au contact, the observed behavior was either characteristic of a resistor or a diode, indicating conductance through the CNT from both the Au and Al pads.

I. INTRODUCTION

SINCE their discovery in 1991, carbon nanotubes (CNTs) have been studied for applications ranging from improving the tensile strength of polymers to nano-scale transistors. In electronics, a carbon nanotube can be categorized as either semiconducting or metallic properties, a property which is determined by its axial configuration. In addition, carbon nanotubes can be classified as a single-walled CNT or a multi-walled CNT, a condition where tubes share the same axis but have different diameters. These interesting electrical properties of CNTs have raised the possibility of their use in a variety of sensors, including one that would use a CNT device to test for the presence of various gases in the air. This work focuses on fabricating and testing a CNTFET device architecture to determine if it could be used for gas sensing applications. Optimally, this sensor would be smaller and more portable than current gas sensors and would allow for gas detection in any condition.

This sensor would operate by exploiting two interesting electrical properties of carbon nanotubes: the semiconducting properties of CNTs and their changing doping level in response to different gases. As a semiconducting CNT is exposed to a gas, the gas adsorbs onto the surface of the nanotube, changing its doping profile and density of states (DOS), which resulting in a different charge on the CNT. By measuring the change in capacitance, one can determine the doping change in the CNT and correlate this information to gases present in the air. This particular device uses a FET architecture (fig. 1) in order to measure the capacitance between the FET gate and the CNT channel.

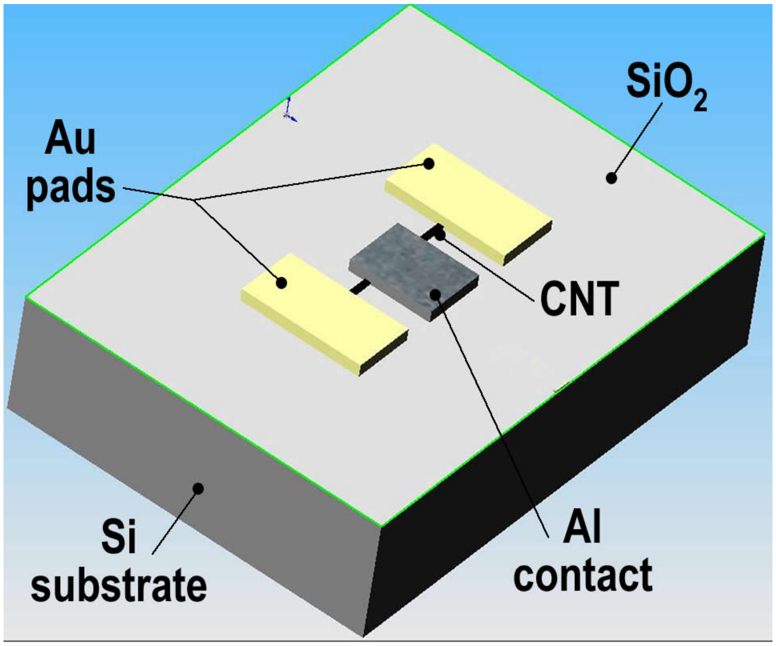

Fig. 1. A 3-D CAD model of the fabricated CNT device

II. DEVICE ARCHITECTURE AND FABRICATION

The nanotubes were grown from Fe catalyst onto a degenerately doped Si/SiO$_2$ (500 nm) substrate using chemical vapor deposition. The substrate was then observed with a scanning electron microscope (SEM) to assure that the nanotubes were grown at the correct density. Approximately two CNTs were visible at 1000x magnification, which is a good density for fabricating single-CNT devices. Alignment markers were patterned onto the CNTs using e-beam lithography, then a 5 nm layer of Cr and a 50 nm layer of Au was thermally deposited to form the alignment markers. The excess Cr/Au was lifted off using an acetone soak.

After patterning alignment markers, Cr/Au contacts were drawn with reference to the alignment markers and CNTs using a CAD program (fig. 2). After patterning the Cr/Au contacts using e-beam lithography, source and drain contacts were placed onto the substrate through thermal deposition of 5 nm of Cr and 70 nm of Au. Cr was chosen as an adhesion layer to assure a good contact between the Au pads and the substrate, and Au was chosen due to its ability to create a p-type CNT device. To form the Al contacts, a third e-beam lithography step was performed and 80 nm of Al deposited. The excess Al was lifted off using another acetone soak to form the completed device (fig. 3). Al was chosen as a second contact metal due to its ability to form Al_2O_3 when deposited in the presence of oxygen. This oxide layer between the Al contact and the CNT would be used to form the capacitor dielectric [6]. In total, four working devices were fabricated.

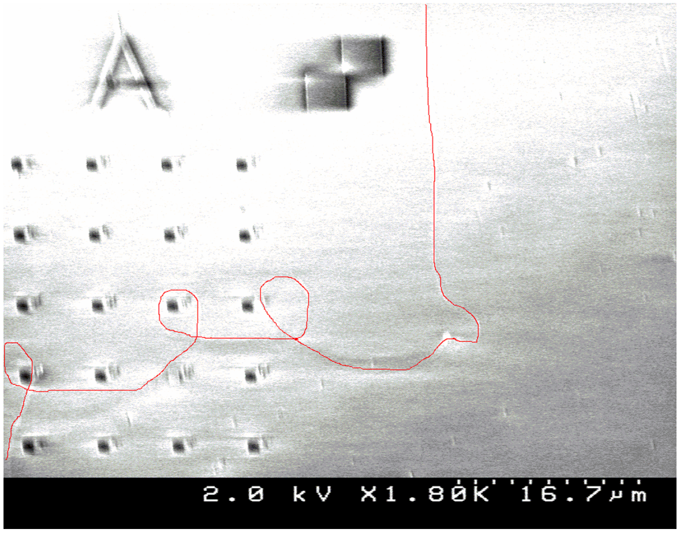

Fig. 2. Alignment markers with CNT shown in black

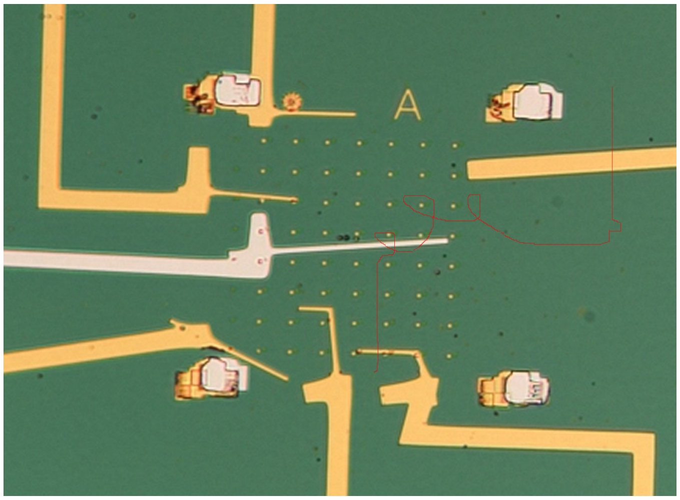

Fig. 3. Device with Au and Al contacts

III. EXPERIMENTAL SETUP

In order to make measurements, the device was either connected to a Desert Cryogenics measurement probe station by one Al and one Au contact to make I-V curve measurements, or by both Au contacts and the back gate contact to record I-V_G back gate curves. A trans-impedance amplifier and a DAQ card were used to acquire voltage and current information from the probe station.

The first measurements were performed before aluminum deposition to make sure that the CNTs were functioning. It was tested in FET configuration by attaching the Au pads to two probes to serve as the source and drain contacts and by attaching a third probe to the doped substrate to act as a back gate. A range of small bias voltages was applied between the source and drain contacts while the back gate voltage (V_G) was swept from -10 V to 10 V in order to observe the gate-dependent behavior of the devices. The conductance curves obtained from this set of measurements gave a preliminary look into what types of CNTs the devices were composed of and what the CNT band-gaps might be.

The second set of measurements was taken to determine if capacitance measurements could be performed. One probe was attached to a gold contact while the other was attached to an Al contact and then a small range of voltages was applied. If no conductance through the nanotube was shown, this would indicate the presence of an oxide layer beneath the Al contact, and the device would be suitable for capacitance measurements.

IV. RESULTS AND DISCUSSION

A. Transfer Characteristics Using Doped Si Back Gate

The results for I-V_G data taken from four devices A1, B1, C1 and C2 are shown in figures 4, 5, 6, and 7. All three I-V_G curves show hysteretic behavior, indicating that there may be charge traps present in the substrate. Device A1 (fig. 4) showed strong p-type conductance behavior for applied gate voltage. It is likely that the device contains semiconducting CNTs, although the non-zero turnoff current suggests the presence of metallic nanotubes. The higher current level at negative voltages can either be the result of ambipolar CNTs or metallic CNTs.

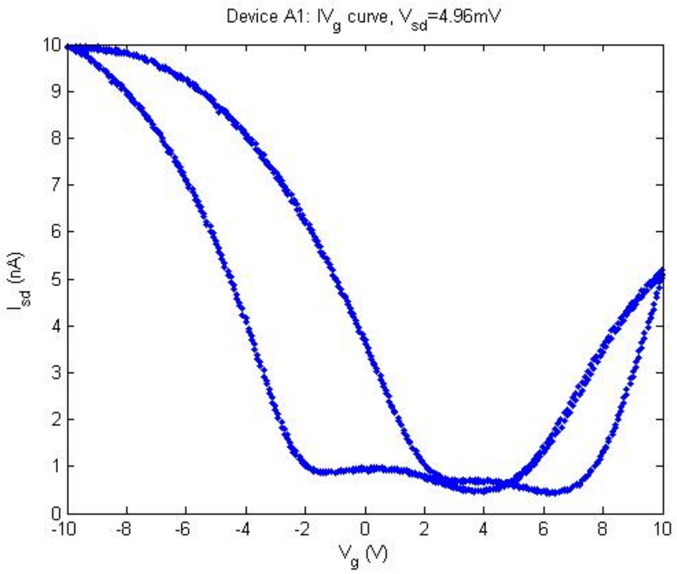

Fig. 4. This device shows a much higher level of conduction for negative V_G.

Device B1 (fig. 5) showed the most interesting transfer characteristics of the three devices. It conducts for both positive and negative gate voltages, indicating that it is an ambipolar device. However, it does have a higher level of

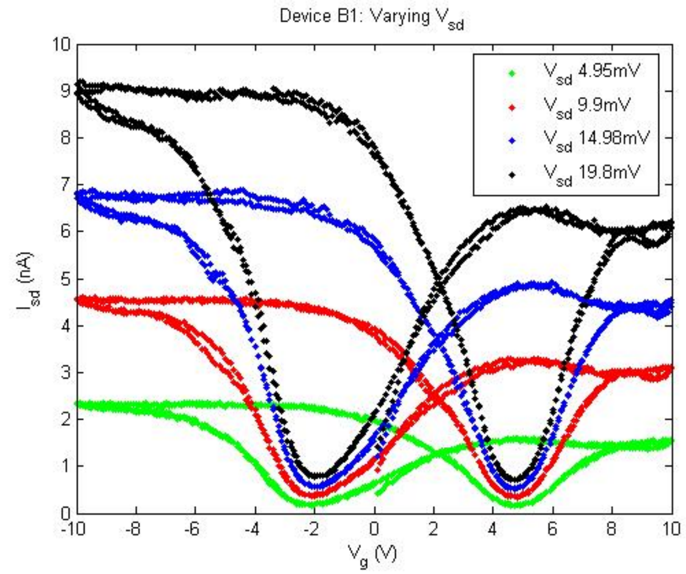

Fig. 5. Device B1 shows a high level of conductance for both negative and positive V$_G$, indicating strong ambipolar behavior.

conductance at negative voltages, indicating that it is more strongly p-type than n-type. The device has a non-zero turn off current, so it is likely that metallic CNTs are present.

Device C1 (fig. 6) behaves differently from devices A1 and B1 by decreasing conductance as voltage increases. The current on the ends of the voltage range is likely due to metallic tubes, while the higher level of current in the middle of the voltage range can be attributed to both metallic and semiconducting CNTs.

Device C2 (fig. 7) shows behavior most consistent with a traditional FET device. It has a high level of conductance at large negative voltages, indicating that it is p-type, but has a low level of conductance for any positive voltage. The current at positive voltages is likely due to metallic tubes while the current at negative voltages is due to both semiconducting and metallic tubes.

B. Device Response to Applied Bias Voltage

The next set of results show the CNT response to an applied voltage between one Au contact and one Al contact. Each device shows significant conductance to the Al top gate, so it is likely that either a very thin or non-existent Al_2O_3 layer formed. Capacitance measurements were not performed on these devices. Device B1 (fig. 8) showed diode like behavior when given an applied bias. This may be due to a Schottky barrier formation between the Al contact and the CNT. One important consideration in this device's behavior is material's work function, or the minimum energy needed to move a charge carrier from inside to directly outside the material. The work functions of Au, CNT, and Al are 5.2 eV, 4.9 eV, and 4.27 eV respectively. Au has a higher work function than the CNT so it does not form a Schottky barrier. However, the Al contact has a smaller work function, causing a large barrier height. This barrier prevents the device from conducting for negative applied bias voltages, unless the bias voltage is negatively large enough to overcome the barrier height. Device C2 (fig. 9) is most likely composed of metallic nanotubes. The non-linear but symmetrical response to applied bias shows that no Schottky barriers have formed between contact metal and CNT. This device likely has a multi-walled CNT with both metallic and semiconducting CNTs.

The Shockley diode equation $I=I_o(e^{\frac{qV}{nk_BT}}-1)$ can be used to predict the I-V behavior of diodes and was used to model the applied bias behavior of devices B1 and C2. In this equation, I_o is the saturation current, q is the

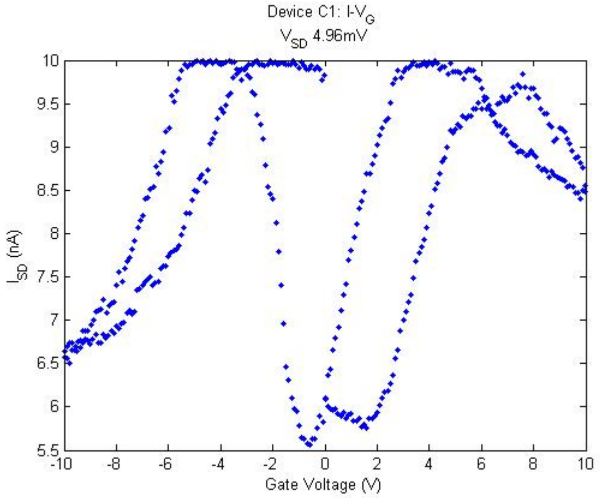

Fig. 6. Device C1 shows unique I-V$_G$ behavior by decreasing conductance as applied V$_G$ becomes larger.

carrier charge, k_B is Boltzmann's constant, and n is the ideality constant, a variable that determines the purity of the semiconductor. N ranges from a value of 1 to 2, with one being closest to a pure PN junction and 2 indicating a very impure semiconductor. The modelled results from device B1 (fig. 10) show what kind of junction it closely approximates. Although the model does not follow the initial path of the data well, as current increases the model more closely follows the data. It is unclear if the ideality constant value is due to deposition conditions of the Al or if it is an inherent property of the CNT-Al junction.

C. Atomic Force Microscopy of CNT Devices

After total device failure, two of the four devices were examined to determine their diameters. By using the equation $E_{bg} = .7/d_{CNT}$ the approximate band gap of the CNT can also be determined. Device A1 shows a diameter of about 5.145 nm and a corresponding band gap of 0.14eV. Device B1 shows a diameter of approximately 3.822 nm and a slightly higher band gap of 0.26eV. The AFM images show that both devices A1 and B2 have fairly large CNTs and are likely multi-walled nanotubes, which would explain the ambipolar semiconducting behavior in the I-V$_G$ curve.

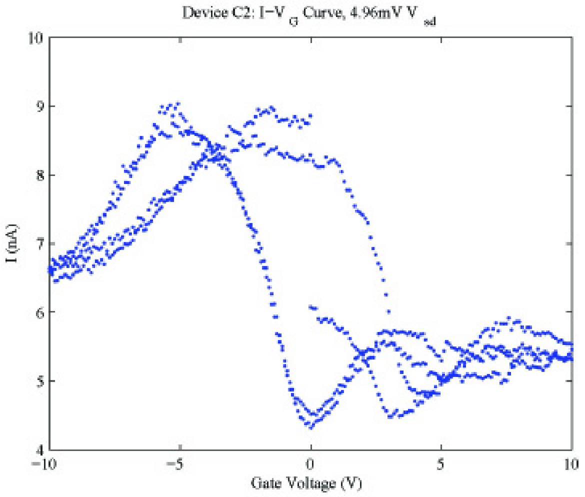

Fig. 7. Device C2 shows decreasing conductance as voltage increases.

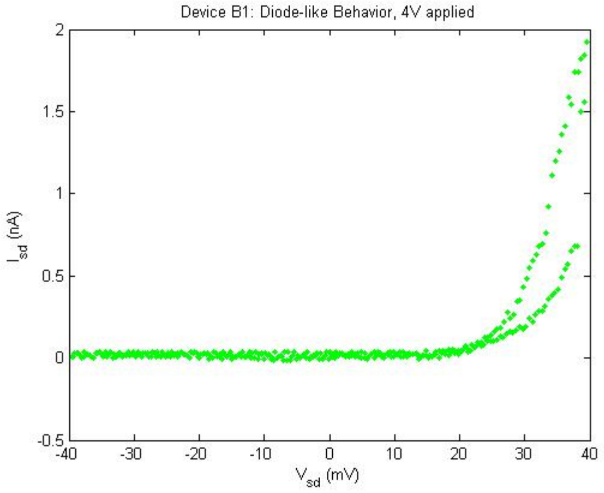

Fig. 8. The I-V behavior for B1 is diode like, with very low conduction for reverse applied bias and high conductance for forward applied bias. The turn-on voltage of this device is approximately 20mV. The data for reverse current is too noisy to obtain a clear value.

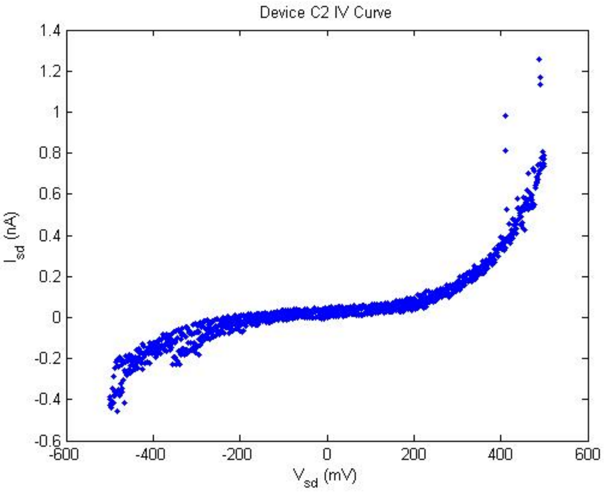

Fig. 9. Device C2 shows a non-linear conductance response to applied bias, indicating that it may contain metallic CNTs. Since the conductance is roughly symmetric around 0V, this device either has a very low breakdown voltage or does not exhibit semiconducting properties.

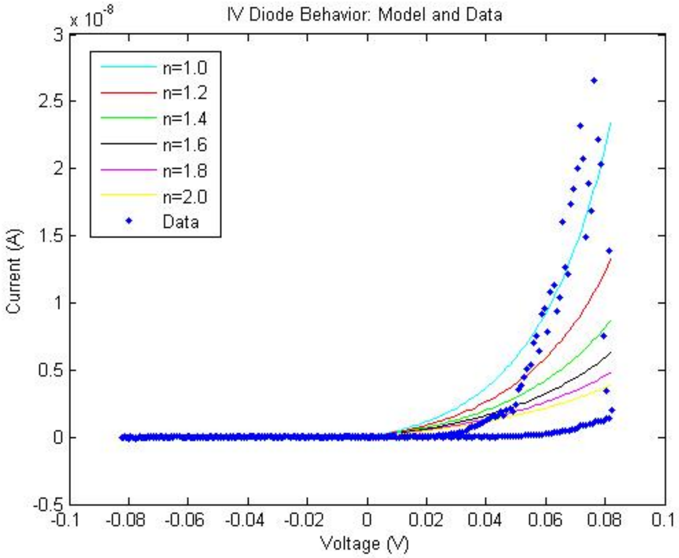

Fig. 10. The model shows a fit to the diode-like behavior best at an ideality constant of n=1, indicating that this device closely approximates a PN junction.

V. CONCLUSION

From the results above, it is clear that different CNT compositions will yield very different device behaviors. It is difficult to generalize behavior or estimate the success of a CNT device because of the variance in CNT properties.

It is unlikely that the device architecture described in this paper would work as a capacitive sensor. The oxide layer between the Al contact and the CNT is too thin to effectively work as a dielectric. It might be possible to explore the current response of CNT devices exhibiting diode-like behavior in order to use it as a gas sensor. It would be interesting to explore the response of these devices to temperature and gases as further work.

Another potentially interesting further exploration of these results would be to fabricate a device using Al as contact metals in order to create an N-type transistor. Normally CNTFETs are P-type, but with the difference in work function between the CNT and Al, it may cause the CNT to become N-type. This could open up a new ability to create logic devices using both P and N-type CNTFETs.

Although it is unlikely that this device architecture could be used as a capacitive gas sensor, these devices may have more applications. One potential use of CNT Schottky diodes would be as a detector in the terahertz range, for use in high frequency systems [2]. Since their diode behavior can be ideal, they can also be used in power conversion applications [1].

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