

Rapid Fabrication of CNT Sensors Using Electro-chemical Deposition of Functionalized CNTs

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Abstract— We present a novel fabrication technique to fabricate functionalized CNT sensors rapidly using electro-chemical deposition method. The basic fabrication process of this sensor includes fabrication of a gold (Au) microelectrode array by photolithography process, functionalization of multi-walled carbon nanotubes (MWNTs) with carboxylic acid groups (-COOH), and electro-chemical deposition of functionalized MWNTs (f-CNTs) on the Au microelectrode array. The adhesion between the f-CNTs and the Au microelectrodes could be enhanced if CNT sensors are built using the process described in this paper. The I-V characteristics of the sensors were investigated. Our experimental results show that CNT sensors fabricated by electro-chemical process have dramatically different I-V characteristics compared with sensors fabricated by DEP or AFM manipulation techniques. The power limit of the sensors ranges from 0.28mW to 6.21mW, which is much higher than most reported CNT sensors. Self-heating effect can be induced at input power of ~2.2mW. Based on these experimental results, we think that the novel f-CNT sensors should be investigated further for applications in thermal, mechanical, and biomedical systems.

Keywords- carbon nanotubes; electro-chemical deposition

I. INTRODUCTION

Carbon Nanotubes (CNTs), since its discovery by Iijima in 1991 [1], are getting more attention due to their promising structural, mechanical, and electrical properties. Since the electrical property of CNTs is a strong function of their atomic structure and mechanical deformations, such relationships make them useful when developing extremely small sensors that are sensitive to the chemical, mechanical, or physical environment. Thermal [2], pressure [3], and chemical [4] sensors were successfully built in the past few years, but, due to the weak adhesion between the CNTs and the substrate, most CNT sensors can only operate in static environment. With the rapid development of microfluidics in recent years, CNT sensors could become a strong candidate if they can operate in dynamic liquid media.

Typical CNT deposition techniques include growing CNTs directly onto substrate by chemical vapor deposition (CVD) [5], printing [6], and thermal spraying [7]. However, these processes usually run in high temperature, which limits the

material of the substrate. In addition, catalysts and other contaminants would be deposited together with the CNTs. Recently, our group has developed a technique by utilizing AC dielectrophoretic (DEP) force to manipulate CNT bundles across Au microelectrodes [2]. An alcohol sensor [9] was successfully built by using this technique. However, the adhesion between the CNT bundles and the Au microelectrodes is relatively weak or limited to physisorption through most probably van der Waals attraction.

In this paper, we will present a novel technique to deposit CNT bundles chemically rather than physically. The CNTs were first functionalized with COOH groups in order to make the chemical reaction between the CNTs and the Au microelectrodes feasible. The CNTs were then deposited electro-chemically. The adhesion between the CNTs and the Au microelectrodes can be improved due to the chemical interaction. In addition, I-V characteristics and the power limit of the sensors will be presented in the later sections.

II. SENSOR FABRICATION

A. Fabrication Process of CNT Sensor Chip

The fabrication process for the CNT sensor chip is shown in Figure 1. Polymethylmethacrylate (PMMA) was chosen as the substrate material because it is optically transparent, biocompatible, and low-cost. A layer of Parylene C was first deposited on the PMMA substrate to protect the PMMA substrate and improve the adhesion of gold (Au) to the substrate. Then, an array (19 in total) of Au microelectrodes were evaporated on the substrate by sputtering and patterned by photolithography process. Since the electro-chemically deposited CNTs would deposit all over the Au layer including the bonding pads and connecting wires, a layer of Parylene C was deposited and patterned on the Au electrodes so as to limit the CNTs deposited only across the Au microelectrodes. A prototype CNT sensor chip is shown in Figure 2.

B. Preparation of Functionalized MWNTs

The multi-walled carbon nanotubes (MWNTs) have to be functionalized with carboxylic acid groups (-COOH) first in order to make the chemical reaction between the CNTs and the Au microelectrodes feasible in the deposition process. The functionalized MWNTs (f-CNTs) were prepared by the following process. Commercial MWNTs with a nominal

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diameter 10-20nm and length of 1-2 μ m (Shenzhen Nanotech Port Co. Ltd.) were used. They were first purified by heating in a box furnace at 400 $^{\circ}$ C for 2 hours under ambient air environment. Then, they were functionalized intentionally by a H₂SO₄ and HNO₃ mixture (v/v 3:1) for at least 24 hours to give CNTs functionalized with COOH groups. Functionalized CNTs were subsequently collected by centrifuging and rinsed by de-ionized (DI) water for several times in order to completely remove the residual acids. They were then further rinsed in methanol, and finally re-suspended into propylene carbonate (PC) (Aldrich; 99.7% anhydrous). The concentration of functionalized CNTs was kept at 0.15mg/ml and the pH was slightly less than 7.

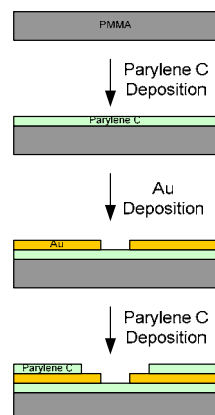


Figure 1. Fabrication process for the CNT sensor chip.

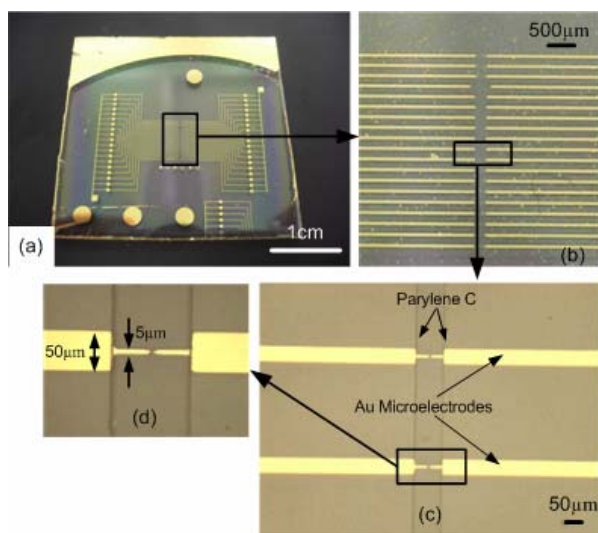


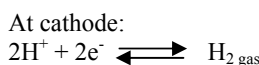
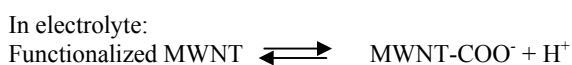
Figure 2. (a) Photograph of a CNT sensor chip; (b) optical microscope image showing an array of Au electrodes; (c)-(d) optical microscope images showing microelectrodes.

C. Electro-chemical Deposition Process of f-CNTs

A schematic diagram of the electro-chemical deposition set-up is shown in Figure 3. The electro-chemical deposition was performed using Gamry 3100 potentiostat with a voltage resolution of 0.01mV and current sensitivity limit of 1nA. Surfactant was added to the f-CNTs electrolyte in order to improve the dispersity of f-CNTs. The fabricated PMMA substrate was attached at the anode and a graphite rod was attached at the cathode, which acted as a counter electrode. A silver/silver nitrate (Ag/AgNO₃) electrode was used as a reference electrode, so that accurate and absolute potential applied to the system could be measured.

During deposition, a positive voltage was applied (with reference to the reference electrode) on the substrate (anode) which is 1.5cm away from the graphite rod (cathode). The electric field applied was always kept below 2V/cm. The duration of the deposition process was about 5 minutes. The sensor chip was then dried in an oven at 70 $^{\circ}$ C overnight to evaporate the residue solvents and impurities.

Electrochemical reactions took place between the electrodes and the electrolyte according to the following chemical half equations:



A series of photos showing the bridging of f-CNTs across the Au microelectrodes is shown in Figure 4.

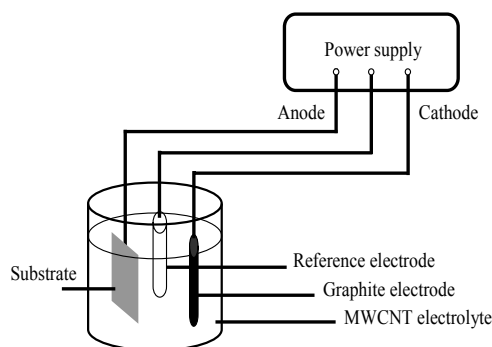


Figure 3. Schematic diagram showing the experimental set-up for electro-chemical deposition of f-CNTs.

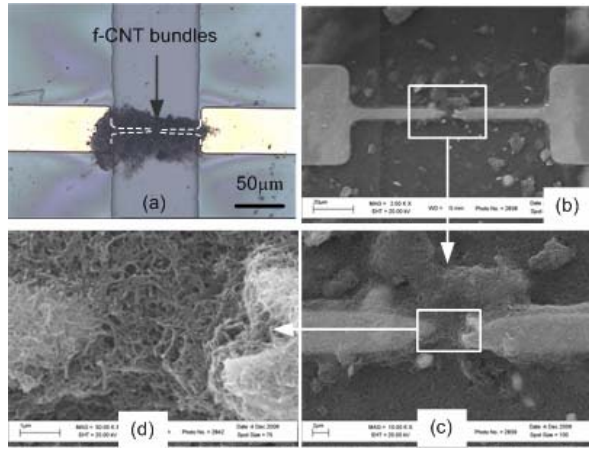


Figure 4. (a) An optical microscope image showing the CNT bridge across the Au electrodes. (b)-(d) SEM images showing the formations of f-CNTs between Au microelectrodes. Note: part of the electrodes are covered by Parylene C.

III. EXPERIMENTAL RESULTS

The formation of f-CNTs linkages can be confirmed by testing the conductivity between the pair of microelectrodes. For instance, room-temperature resistances between the microelectrodes were measured and the two-probe room-temperature resistances of the samples typically range from several hundred ohms to several kilo ohms, which are much smaller than the CNT sensors fabricated by DEP technique (resistances from several to several hundred kilo ohms). We further validate the existence of f-CNTs by Raman spectroscopy. The Raman spectrum of the sample is shown in Figure 5. A peak feature is observed around 1580cm^{-1} , which is the tangential band or so called the G band (from graphite) [8]. Based on these results, we proved that CNTs were present in the sample.

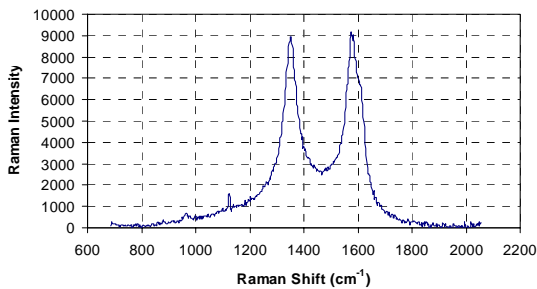


Figure 5. Raman spectra of electro-chemically deposited CNT sensor.

A. IV Characterization

Our group has previously investigated the electrical property of bare CNT sensors [2] and f-CNT sensors [9]. We proved that self-heating effect started at $\sim 1\text{V}$ for both bare CNT sensors and f-CNT sensors, which suggested that bundled CNTs could be used as a resistive element for ultra-low-power consumption. In this study, we examined the I-V characteristics of the electro-chemically deposited f-CNT

sensors using a constant current configuration. Three sensors (sensor #1, #2, and #3) with similar resistances (197.7Ω , 201.7Ω , and 291Ω , respectively) were tested and the results are shown in Figure 6.

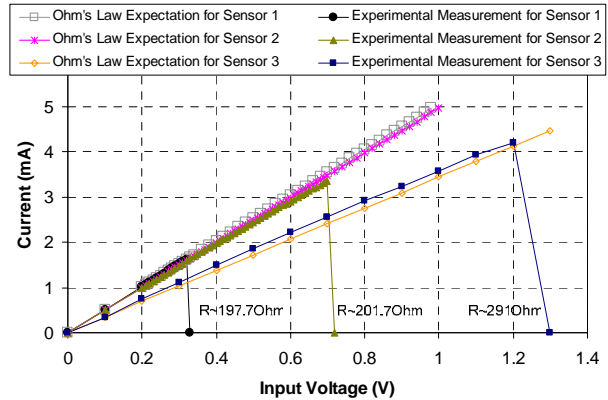


Figure 6. I-V characteristics of the f-MWNT sensors. Three sensors were tested. The theoretical expectations using Ohm's law of each sensor were also plotted for comparison.

The output current responded linearly when the input voltage started increasing, but suddenly dropped to nearly zero, i.e., the resistance increased enormously to several mega ohms. The current dropped at different voltages for different sensors and the corresponding power input were 0.52mW , 2.34mW , and 5.02mW , respectively, when the sensors apparently were "burnt" out. However, very interestingly and for reasons we could not explain at this time conclusively, the room-temperature resistances of the sensors then went back to several hundred ohms after a few minutes time. But, they could not go back to the original resistance. We will perform further investigations of this phenomenon and give a conclusive report in the future.

Several cycles of I-V measurements were done on each sensor to determine the power limit of each sensor and the results are shown in Figure 7. The power limit of the sensors ranged from 0.28mW to 6.21mW , which the values varied with individual sensor. On the other hand, for each individual sensor, the power limit became smaller with a larger resistance. The results are consistent with all three sensors. This agrees with our previous study that CNT sensors can operate at a very large power range (μW to mW) [10].

Besides the power limit, the break down voltage of the sensor was also investigated. Three cycles of I-V measurement were performed on sensor #3 with three different room-temperature resistances (490Ω , 291Ω , and 254Ω) and the break down voltages are shown in Figure 8. Although the room-temperature resistances were different, the break down voltages were very close (between 1.3V - 1.5V). This shows that the break down voltage does not depend on the room-temperature resistance, but the sensor has its own break down voltage.

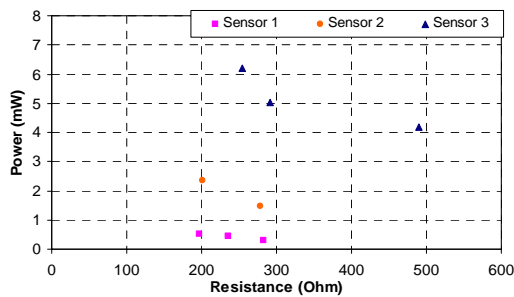


Figure 7. Power limit of three sensors with different room-temperature resistances.

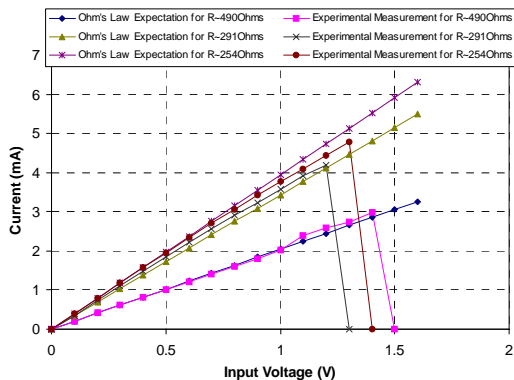


Figure 8. I-V characteristics of sensor #3. Three measurements were done with different room-temperature resistances. Results show that the break down voltage ranges from 1.3 to 1.5V.

To further validate the electrical properties of the sensors, an I-V measurement was carried out on sensor #4, which has a higher room-temperature resistance of $\sim 11.2\text{k}\Omega$. The results are shown in Figure 9. The results are similar to the DEP fabricated CNT sensors reported in [2]. However, self-heating effect started at 0.2mA and 2.2V, which is at a power input level an order of magnitude higher than DEP fabricated CNT sensors. The self-heating effect continued until the input voltage reached 4.2V, when the current dropped significantly. The corresponding power consumed was 2.2mW. Since the room-temperature resistance of sensor #4 was larger, it could reach a higher voltage with less power consumed than sensor #3.

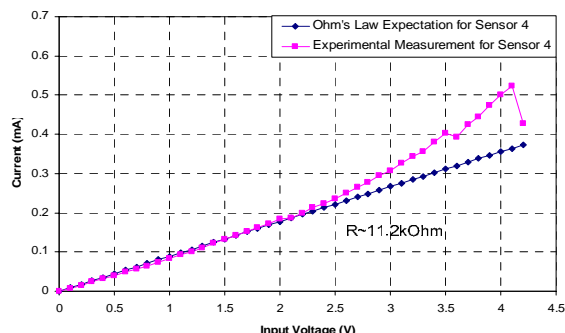


Figure 9. I-V characteristics of sensor #4. The straight line is the theoretical expectation using Ohm's law and the room-temperature resistance of the sensor was approximately 11.2kOhms.

IV. CONCLUSION

A rapid fabrication technique to batch fabricate functionalized CNT sensors based on electro-chemical deposition has been successfully demonstrated. MWNT bundles were aligned between Au microelectrodes by chemical reaction in only 5 minutes. The room-temperature resistance of the sensors is only several hundred ohms, which is much smaller than the DEP fabricated CNT sensors. The f-CNT sensors were tested for I-V characteristics and were proved to be operable at mW range. The sensors broke down at a certain power, which the value was sensor dependent. The power limits of three sensors were investigated. For each individual sensor, the power limit decreased as the room-temperature resistance increased. Also, we found that each individual sensor has its own break down voltage regardless of its resistance change. Finally, a sensor with a resistance of $\sim 11.2\text{k}\Omega$ was shown to have self-heating effect with power input of $\sim 2.2\text{mW}$. These experimental results give us the basic I-V properties of the electro-chemically deposited f-CNT sensors, which serve as guideline to further improve our fabrication process before exploring their applications in real applications.

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