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Single-Walled Carbon Nanotube based pH Sensors on a Flexible Parylene-C Substrate

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***Abstract*—In this paper, we present a suspended Single-Walled Carbon Nanotube (SWNT) based pH sensor utilizing a low temperature Dielectrophoretic (DEP) assembly process on a flexible parylene-C substrate. Parylene-C, a light weight, flexible and inert material, is compatible with many microfabrication processes. Furthermore, utilizing parylene-C as a flexible substrate, one can readily create a suspended microplatform utilizing an O_2 plasma etch process. Suspended nanobridges have larger exposed surface areas and may potentially have enhanced sensitivity for sensing applications. Fabricating these structures on a thin (10μm) parylene-C substrate allows their utilization as flexible devices or in wearable sensor applications. We have successfully assembled suspended SWNT nanobridges across a spacing of 4μm. The electrical characterization results from the assembled SWNTs yield ohmic behavior with a measured two-terminal resistance of ~17KΩ. Furthermore, the conductometric measurements of the SWNT sensors have demonstrated that corresponding to an increase in pH value, the resistance of SWNTs has decreased due to the OH^- group that attached on to the wall of the SWNTs and changed the electrical properties of the SWNTs. These novel suspended nanostructures can be used as potential candidates in nanosensor applications.**

I. Introduction

PH sensors are of great importance in a wide range of applications including clinical analysis, environment analysis and process control [1, 2]. A miniature pH sensor is of particular interest in the field of medical diagnostics for use on catheter tips or in implantable devices. For instance, a pH sensor can be used to diagnose a disease through blood and to detect environmental pollution through water. Single-walled carbon nanotubes (SWNTs) are promising candidates as active materials in sensor applications due to their small size, large surface area-to-volume ratio and fast response. The electronic properties of SWNTs are strongly related to the atomic structure and mechanical deformations which make them useful when developing extremely small sensors that are sensitive to the environment. Several CNT based sensing devices have been reported including mechanical sensors [3], gas sensors [4, 5] and biological [6] and chemical sensors [7]. Theoretical studies have shown significant changes in the electronic properties of SWNTs due to the hydroxide ions (OH^-) in the pH solution [1]. Due to the attachment of the OH^- group on the walls of the SWNTs in the buffer solutions, the changes in the conductivity of the SWNTs shows that it can be a promising candidate as a pH sensor. Previously, several groups have investigated CNT based pH sensors [1, 8-10] however, none of them were fabricated on biocompatible polymeric substrates which are relatively inexpensive and disposable.

In this paper, we present a SWNT based pH sensor fabricated on a flexible parylene-C substrate. Furthermore, parylene-C is a biocompatible material and can be used for medical and implantable device applications [11]. Utilizing Dielectrophoretic (DEP) assembly process, we assemble the SWNTs onto a prefabricated microplatform and fabricate suspended SWNTs. DEP assembly process has been shown to control the manipulation and trapping of micro- and nanomaterials at room temperature [12]. Compared to sensing structures residing on a substrate, suspended nanobridges have larger exposed surface areas and may potentially have enhanced sensitivity for sensing applications. Besides, utilizing parylene-C as a substrate, one can simply use dry etching processes (O_2 plasma etching) to create a suspended microelectrode pair. Here, suspended structures that were about 1μm above the substrate were fabricated with the gap of ~4μm. Fig. 1 shows the array of microplatforms fabricated on a flexible parylene-C substrate. This versatile technique allows the realization of nanosensors with potential applications in disposable and implantable devices for medical diagnostics.

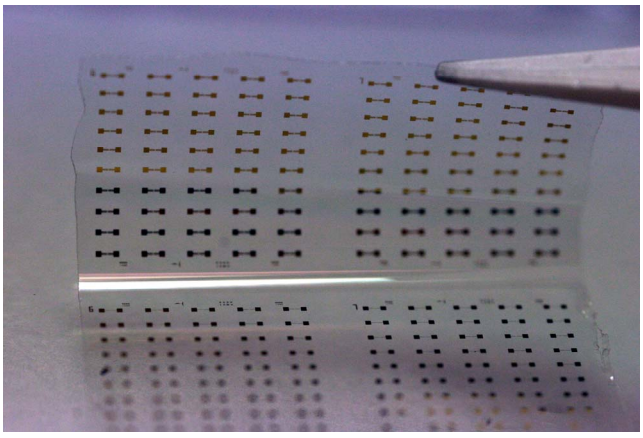

Fig. 1: Optical photograph of the array of micromachined platforms fabricated on a flexible parylene-C substrate.

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II. Material Properties and Fabrication Process

Parylene, poly-para-xylylene, is the generic name for members of a unique polymer series and has 20 variants where parylene N, C, F and D are the most commonly used types. In this work, parylene-C has been utilized as a flexible substrate due to its attractive properties which include a lightweight, stress-free and mechanically strong material. Compared with most commonly utilized flexible substrates such as poly(ethylene Naphthalate) (PEN), poly(ethylene terephthalate) (PET) and polydimethylsiloxane (PDMS), parylene-C is compatible with standard microfabrication methods and can be fabricated with thicknesses down to several microns. Besides, it has a high Young's Modulus (~3GPa) [13] and high tensile strength (70MPa) [14] which allows utilization of very thin layers (down to 5µm) compared to other flexible substrates. Despite its advantages only a handful of investigators have utilized parylene-C as a flexible substrate [15-18].

Parylene-C is deposited at room temperature under low vacuum conditions (around 0.1 Torr). The mean free path is on the order of around 100µm, which results in a conformal coating on the substrate. Compared with vacuum metallization, the deposition rates of parylene-C are fast and its thickness can be easily varied by the amount of dimer placed inside the reactor. Conventional flexible substrates are purchased in sheet form which are not convenient to build devices upon. In our case, we utilize silicon as a handle substrate to hold the thin parylene layer during processing and simply peel off the parylene film after completing the fabrication steps. Besides, by utilizing a dry etch process (O_2 plasma etching), we have demonstrated a suspended microplatform for SWNT assembly and created planar suspended SWNT structures which have enhanced surface area for sensing.

A. Dielectrophoretic Assembly

One technique that has been shown to control the manipulation and trapping of micro- and nanomaterials at room temperature is Dielectrophoretic (DEP) assembly [12]. Due to its versatility and flexibility, it is increasingly being utilized during incorporation of nanomaterials including nanotubes, nanowires and nanoparticles on to devices. Dielectrophoresis (DEP), coined by H. A. Pohl [19], refers to the force exerted on the induced dipole moment of small nanomaterials suspended in insulating dielectric liquids by a nonuniform electric field. When a nonuniform electric field is created by applying a voltage to the electrodes, the suspended nanoparticles will be attracted to the regions of maximum or minimum field intensity. Nanomaterials would respond to both AC and DC electric fields. AC field was utilized in these experiments since it is known to suppress the electrochemical and particle migration effects present during the application of DC fields [20, 21]. Furthermore, DEP has emerged as a powerful method for manipulation and trapping of micro- and nanoparticles [12]. DEP forces can trap single particle on or between electrodes with the appropriate electrode geometry and careful control of the experimental conditions

B. Fabrication Process for the platform

The fabrication process starts by depositing a 10µm thick parylene-C layer on a 3" silicon wafer shown in Fig. 2(a). Conventional optical photolithography followed by a lift-off process is utilized to pattern the Au electrodes on the parylene-C layer (Fig. 2 (b) and (c)). Au electrodes serve as a microplatform for the nanotube assembly process. Finally, a simple dry etching process utilizing O_2 plasma has been performed on the platform to realize suspended electrodes for SWNT assembly (Fig. 2 (d) and (e)). After fabrication, the parylene-C substrate containing the nanotube sensors is carefully peeled off from the silicon substrate (Fig. 2 (e)).

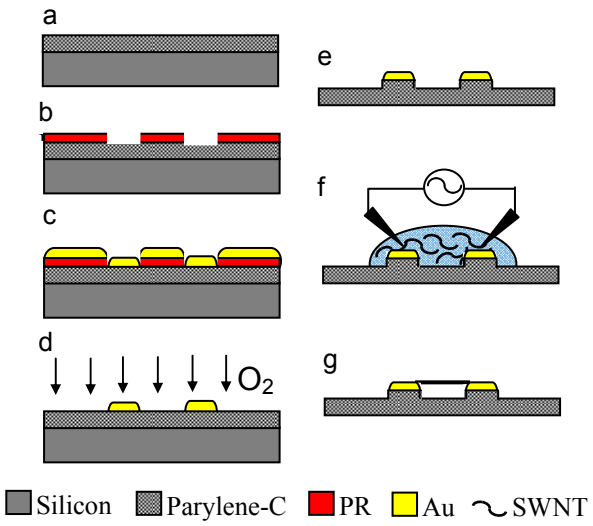

Fig. 2: Microplatform fabrication process (a) deposited 10µm parylene-C as a flexible substrate on 3" silicon substrate. (b) and (c) optical lithography to pattern Au microelectrodes. (d) and (e) O_2 plasma etching to form the suspended structure and then the parylene membrane is peeled off from the silicon substrate to form the flexible device. (f) and (g) DEP assembly to assemble SWNTs.

III. Experimental Results and Discussion

A. Assembly Process and I-V Measurements

In these experiments, an aqueous suspension of highly purified HIPCo-grown SWNTs (Nantero, Inc.) was used with a concentration of 0.004 g/ml, which was diluted using deionized water. The average diameter of the SWNTs used was about 2 nm with an average length of 3 µm. A 3µL SWNT solution was first dispensed onto the microelectrodes of the microplatform and then an AC sinusoidal signal of 2 V_{pp} (peak to peak) at a frequency of 10 MHz (Fig. 2(f)) was applied using a function generator (Agilent 33220A) between the two electrodes to perform DEP assembly. After 20 sec of assembly, the solution was dried with a nitrogen gun and the power is turned off resulting in horizontal suspended SWNTs.

Fig. 3 shows the SEM micrograph of the assembled SWNTs. From the SEM micrograph it is clearly seen that the SWNTs were suspended in between the electrodes with a gap of around 4µm. The height of the microelectrodes was around 1µm after O_2 plasma etching. Fig. 4 shows the two terminal I-V measurements from the assembled SWNTs. The measured resistance is around 17KΩ (Semiconductor Parameter Analyzer, HP 4155).

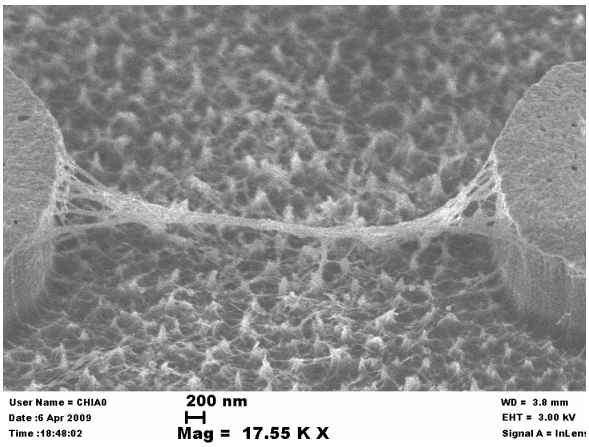

Fig. 3: SEM micrograph of the assembled SWNTs suspended between two electrodes.

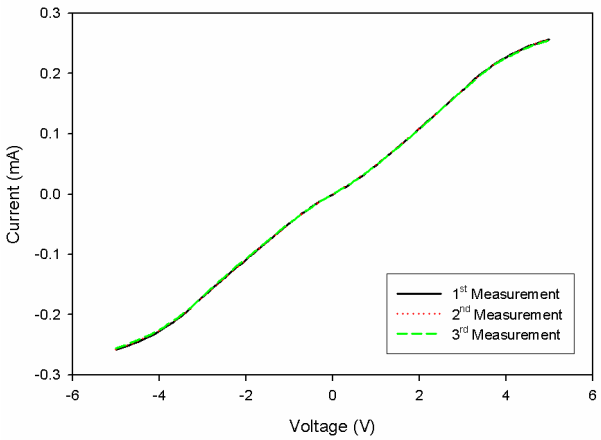

Fig. 4: Two terminal I-V characterizations where the resistance was measured as ~17KΩ.

B. *pH Sensing Measurements*

The pH sensing experiments were performed by measuring the resistance of SWNTs under a probe station (SUSS, MicroTec, PM5) utilizing a multimeter (HP 34401A) with LabVIEW control. The experiments were repeated three times to confirm the reliability and reproducibility. Fig. 5 shows the schematic drawing of the suspended SWNT based pH sensor. In our experiments, we have utilized two different buffer solutions (HACH and Fisher Scientific) with pH 4 (acidic), pH 7 (neutral) and pH 10 (basic). The resistances of SWNTs were measured and recorded every second using LabVIEW program control.

Fig. 6 shows that the recorded resistance values from SWNT vs time measurements from two different buffer solutions. From the data we noticed that the value of the SWNTs resistances from two different buffer solutions was not the same. We believe that it is due to the displacement of SWNTs during testing process. Furthermore, the experiment results indicated that the resistance values of the SWNTs decreased as they were exposed to solutions with higher pH values from both buffer solutions. It has been reported that significant changes in the electronic properties of SWNTs occur due to the interaction between the hydroxide ions (OH^-) in the pH buffer solution and the surface of the SWNTs [1]. Because the OH^- group that was attached on to the wall of the SWNTs, the pH buffer solutions will increase or decrease the conductivity of SWNTs depending on whether the solution is acidic or basic. Furthermore, buffer solutions were made from different chemical components such as potassium ion (K^+), sodium (Na^+). These ions do not react with SWNTs.

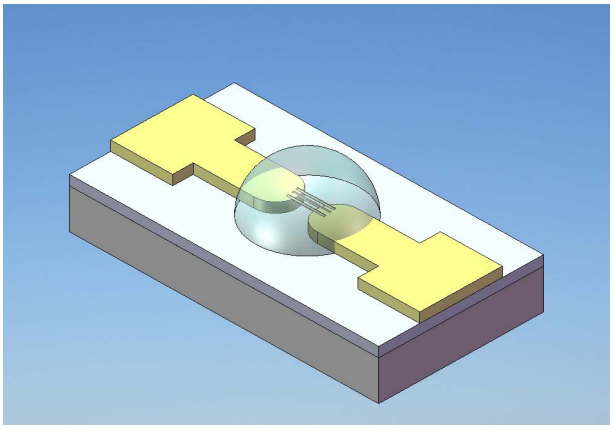

Fig. 5: Schematic drawing of the suspended SWNT based pH sensor.

We also calculated the changes in resistance under different pH buffer solutions (Table 1). For HACH brand buffer solution, the resistance value was 92, 76 and 72 kΩ at pH = 4, 7 and 10, respectively. The decrease of the resistance in percentages was 17.32% from pH 4 to pH 7 and 6.25% from pH 7 to pH 10. For the Fisher brand buffer solution, the resistance value was 101, 86 and 77 kΩ under pH = 4, 7 and 10, respectively. The percentage decrease in resistance was 15.59% from pH 4 to pH 7 and 9.61% from pH 7 to pH 10. We noticed that for both buffer solutions, the resistance decrease trend was very similar. The experimental results also showed that the pH sensor was reproducible. Due to the small standard variation, it also indicated that the SWNT pH sensors were reliable.

TABLE I
SWNT PH SENSING RESULTS

	HACH	FISHER
PH4	(92.32±0.40) KΩ	(101.32±0.27) KΩ
PH7	(76.33±0.18) KΩ	(85.53±0.18) KΩ
PH10	(71.56±0.20) KΩ	(77.31±0.18) KΩ

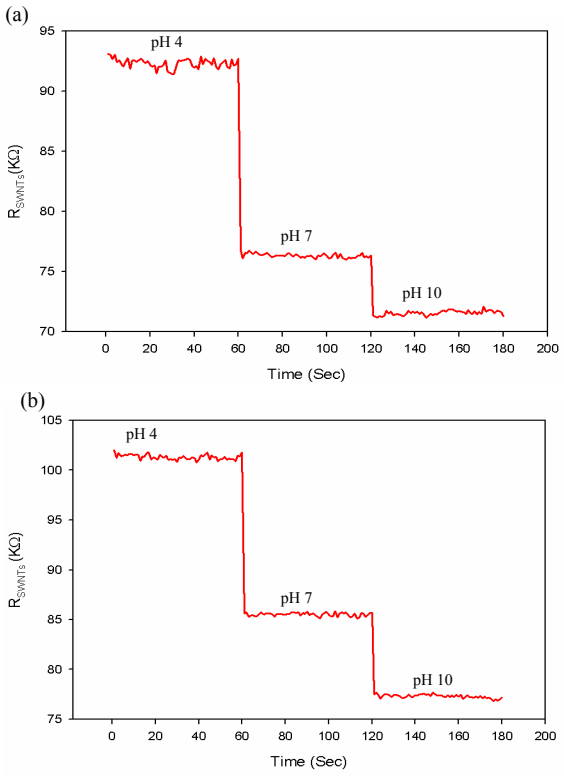

Fig. 6: Measured resistance values from suspended SWNTs vs time measurements (a) Buffer solution was obtained from HACH. (b) Buffer solution was obtained from Fisher Scientific.

IV. Conclusions

We have demonstrated suspended SWNT based pH sensors on a flexible parylene-C substrate. The hybrid fabrication technology combines top down manufacturing (fabrication of the microplatform) and bottom up dielectrophoretic assembly. The assembly process (DEP) is a high yield, low temperature and is scalable to wafer scale fabrication. Next, utilizing this process, a SWNT based pH sensor has been demonstrated. The measurements from the pH response of SWNTs indicate that the change in the concentration of H^+ and OH^- causes an electronic structure change in semiconducting SWNTs by refilling or depleting their valence band. This research allows the realization of novel low cost, disposable nanotube based pH sensors for clinical analysis, environment analysis and process control.

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