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Fabrication of single walled-carbon nanotubes based pH sensor using ultra-precision spray

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Abstract. The concentration of the hydroxyl radical is a critical parameter to be measured for monitoring the condition of aqueous biological species, or for predicting the path of chemical reactions. This paper describes a novel method for fabricating a very simple and fast response pH sensor compose of single walled-carbon nanotubes (SW-CNTs) using an ultra-precision spray. Such CNT-based sensor shows amperometric response in buffer solution at different hydroxyl radical concentrations and electrical conductance of SW-CNTs depends on the pH value. Our results suggest that sprayed CNT sensors are potential candidates as biosensors in future large-scale throughput devices.

1. Introduction

The recent advancement in CNT nanotechnologies has shown great potential in providing viable solutions. CNTs with well-defined nanoscale dimension and unique molecular structure can be used as bridges linking biomolecules to macro/micro-solid-state devices so that the information of bioevents can be transduced into measurable signals [1]. Both the solubility of many chemicals or bio-molecules in solution and the speed or rate of (bio-) chemical reactions are dependent on pH. In order to optimize the desired reaction and to prevent unwanted reactions, controlling the pH of solutions is also very important. Owing to essentially measuring pH in finding the chemical characteristics of a substance, other groups have studied that a single semiconductor CNT [2] or random networks of SW-CNTs [3] used to construct sensing materials in pH-sensitive field-effect transistors (pH-FETs). However, these techniques have complicated and limited controllability, hence are unattractive for scaling up to high-density sensor arrays, since manipulating individual carbon nanotube [4,5] and random dispersion of suspended carbon nanotubes onto prepatterned electrodes are fabricated by lithographically patterning catalyst (as CNT nucleation sites) on electrodes [6,7]. In contrast, sprayed bundled SW-CNTs are easily produced either by direct growth on a catalyzed substrate or by deposition onto arbitrary substrate from a solution of suspended SW-CNTs. To our knowledge, sprayed CNTs based devices have not been used for pH sensor, although sprayed CNTs based applications were used [8,9]. The goal of this work was to develop one of simple mass fabrication methods possible for sprayed SW-CNTs based pH sensor.

2. Experimental

The SW-CNT powder (purchased from Iljin Nanotech Co., Ltd.) had 1-1.2 nm average diameter, 5-20 μm length and ~ 90 % purity (prepared by Arc-discharge process). Prior to the SW-CNT manipulation, 40 mg of the sample was ultrasonically dispersed in 100 mL ethanol solution and the resulting solution was diluted to 0.4 mg/mL or lower concentration for later usage. The fabrication process for the sprayed SW-CNTs based sensor is shown in figure 1. As seen in the fabrication process, SiO_2 was first deposited on the silicon substrate to avoid conduction of the Cr electrode with the substrate. Then photoresist (AZ 7220 photoresist, Clariant industries Ltd.) was spun-on and patterned on the substrate. This photoresist layer can be used as a sacrificial layer for particular applications of the sensors. Afterward, Cr was deposited on the top of the bottom patterned layer and sacrificial layer can be released using etchant (AZ REMOVER 700, Clariant industries Ltd.) to serve as mechanical micro bridges that suspend the SW-CNTs sensor across the Cr electrodes. This gap distance between electrodes for the spayed SW-CNTs is between 5 μm and 6 μm. Based on the technique for CNT manipulation presented in the previous paragraph, the bundled SW-CNTs was manipulated and connected across the microelectrode of each sensor. Finally, bundled SW-CNTs can be dispersed on the shadow mask using an ultra-precision spray (LiPO Functional materials Institute).

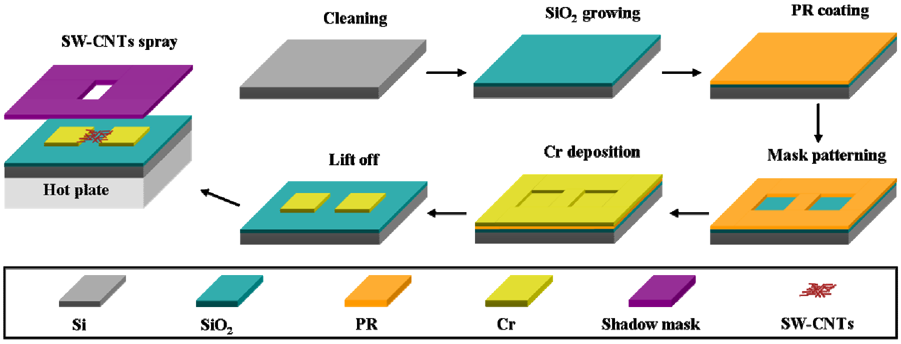

Figure 1. Fabrication process flow for the sprayed SW-CNTs based sensor.

To describe the pH response of bundled SW-CNTs, 0.5 μL of pH buffer solution (Tokyo Kasei Kogyo Co., Ltd.) was used with micro-pipette (Eppendorf Co., Eppendorf Research Pipettes). Real time current measurement was performed using a calibrated Keithley (Keithley Instruments, Inc., 4200 SCS) at room temperature. The surface geometry of bundled SW-CNTs was observed by field emission scanning electron microscope (Hitachi S-4300 unit, FE-SEM).

3. Results and Discussion

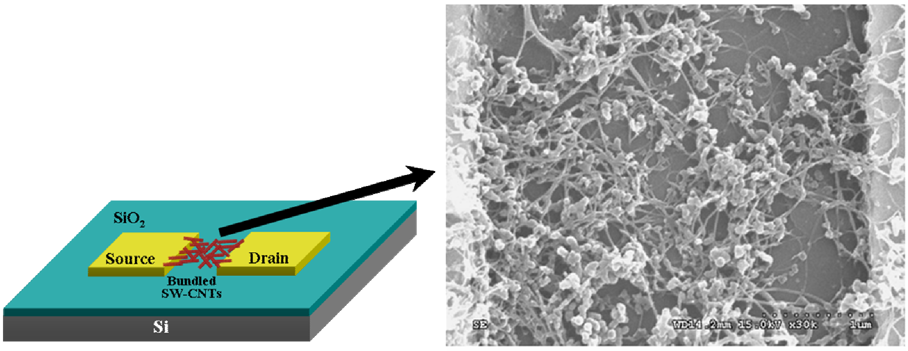

Figure 2. Schematic view of the electronic sensing device consisting of interconnected SW-CNTs bridging two metal electrode pads (left figure). FE-SEM image of SW-CNTs bridging two metal electrode pads on a substrate consisting of randomly overlapped bundles for molecular absorption (light figure).

Figure 2 shows a FE-SEM image of random networks of SW-CNTs in the region between the source-drain electrodes. This gap distance between electrodes is 4 μm. The vine-like morphology of SW-CNTs allows foreign molecules (whether from a gas or a liquid) to readily access nanotubes throughout the entire sensing material via micro- to nanometer-sized vine between these bundles. We experimentally found that room temperature resistances of the SW-CNTs typically range from several kΩ to several hundred kΩ, which depend on their lattice geometries during spray process and weakly side-bonding between bundled SW-CNTs and electrodes created by Van der Waals interaction [10]. Therefore, it is logically that different SW-CNTs exhibited different conductivities.

Figure 3 shows that the conductance of SW-CNTs could be substantially increased or decreased upon exposure to pH buffer solutions. For monitoring the conductance change of SW-CNTs, we used pH 10 and pH 4. In other words, high concentration of hydroxyl radical and low relative concentration of that are measured.

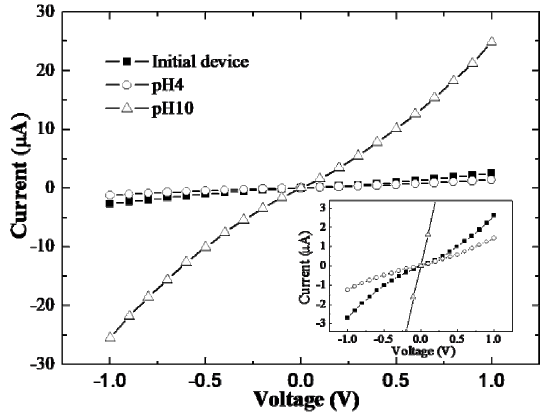

Figure 3. I-V characteristics of bundled SW-CNTs pH sensor at two different pH buffer solutions.

It can be seen from figure 4 that conductance increases with hydroxyl radical concentrations. The changes in conductivity ($\Delta I / \Delta V$, Slope) also depend on pH value. Due to hydroxyl radical attached on the wall of the SW-CNTs, pH buffer solutions could decrease or increase the conductance depending on whether the Fermi level of the metal SW-CNTs contact was placed at a higher or lower energy level than that of bare SW-CNTs.

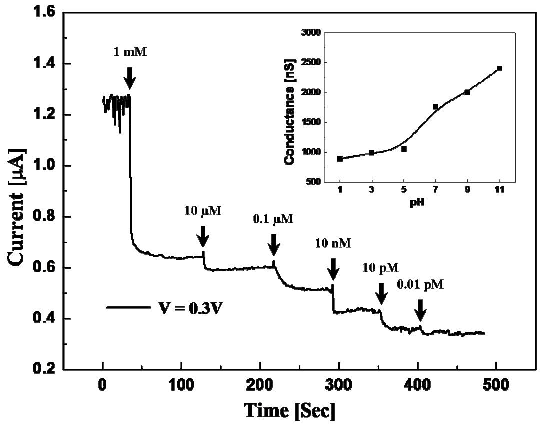

Figure 4. Typical galvanic response of random networks of SW-CNTs at room temperature on the addition of increasing concentrations of hydroxyl radical. The inset shows the conductance of increasing concentrations of hydroxyl radical.

Figure 4 shows real time current measurement of drain current as a function of time for pH sensor by depositing droplet of 0.5 μL pH buffer solutions on bundled SW-CNTs. The response was recorded followed by adding increasing concentrations of hydroxyl radical into the SW-CNTs from 10^{-3}M to 10^{-15}M. The device was exposed to rabbit hydroxyl radical (1 mM) as control for selectivity (1st arrow). Lack of a significant signal after this addition indicated successful blocking of a structurally similar but nonspecific hydroxyl radical concentration. 10 μM was then added, where upon a signal change was observed, indicating a successful binding of OH group to the device pre-adsorbed with OH^- (2nd arrow). OH^- at the 0.1 μM concentration level yielded an additional, relatively proportionate, response (3rd arrow). And other responses were recorded followed by adding increasing concentrations such as 10 nM, 10 pM, and 0.01 pM, respectively for, 4th-7th arrow. Although response properties in less than 0.1 pM are degenerated, it can be seen that the response of the sensor is very fast at ultra-small concentration, thus rendering our device a pH sensor. Also, it can be seen from inset that conductance increases with hydroxyl radical concentrations. These data indicated that is pH value responsible for the measured increase in conductance from 1 to 11. The conductance change is small at low pH range (1 to 5) but large at high pH range (7 to 11). Notably, these pH measurements on SW-CNTs are in excellent agreement with previous measurements of the pH-dependent surface charge density derived from carbon [11]. It can be known from our work that carbon nanotubes has been shown to be very sensitive to ambient condition: charge transfer due to molecular adsorption to the CNT can drastically change the conductance of the device. Namely, the increase in conductance with increase pH is consistent with an increase OH group doping concentration. The OH group does not etch the tube as a result of oxidization. The OH doping can be an effective mechanism for modifying the electronic properties of SW-CNTs, which makes SW-CNTs a possible candidate for gas, oil, and bio-sensor.

4. Conclusion

The present work leads to two important directions of study. First, we present how to fabricate novel pH sensor applicable for mass-production process. Our experimental process flow for pH sensor fabricated by means of an ultra-precision spray can be divided into three parts, which are: 1) fabrication of microelectrodes; 2) sensing material fabrication; and 3) experimental testing. Second, the device is measured by depositing ultra small concentration of hydroxyl radical, and its electrical conductance is monitored while hydroxyl radicals are added to the solution. These results show our technique can be further optimized for increased sensitivity and selectivity for aqueous-phase biosensing. Thus, we forecast this fabrication is very promising technique for electrochemical and gas sensor applications.

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