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MEMS-based fabrication of multi-walled carbon nanotube pH sensor

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Abstract. In this paper, We presents experimental results that demonstrate the pH sensing capability of MW-CNTs. High-density, well-aligned carbon nanotubes, which are MW-CNTs and vertically aligned on a large area of substrate, has been synthesized. The absorption of different range of pH buffer solution in the MW-CNTs changes the conductivity of the MW-CNTs at room temperature. A MEMS-based fabrication process was developed to fabricate a device where MW-CNTs based sensing material was precisely assembled pattern.

Introduction

The recent advancement in carbon nanotube (CNT) nanotechnologies has shown great potential in providing viable solutions. CNTs have a large surface-to-volume ratio and aspect ratio with the diameter of a few nanometers and length up 100μm so that they form an extremely thin wire, a unique one in the carbon family, with the hardness of diamond and the conductivity of graphite. The electronic 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 and mechanical or physical environment. There are two distinct structural families in carbon naotubes, multi-walled carbon nanotubes (MW-CNTs) and single-walled carbon nanotubes (SW-CNTs). MW-CNTs are composed of concentric and closed graphite tubules, each with a rolled graphite sheet, formed with a range of diameters, typically from 2 to 25nm, and the distance between sheets is 0.34nm, closed to the interlayer spacing in graphite. A SW-CNT is made of a single graphite sheet rolled seamlessly, which is an individual cylinder of 1-2nm diameter. SW-CNTs have the tendency to aggregate, usually forming bundles that consist of tens to hundreds of nanotubes in parallel and in contact with each other[1,2].

The unique chemical and physical properties of CNT have paved the way to new and improved sensing devices[2,3]. CNTs based electrochemical sensors offer substantial improvements in the performance of pH sensing device. The measurement of pH buffer solution is one of the most common tasks required in clinical analysis, environmental analysis and process control. In other previous reports related to this issue, applications of carbon nanotubes as pH sensors have been focused either on isolated single-walled carbon nanotubes(SW-CNTs) or on SW-CNT mats[4,5]. SW-CNT is a well-defined system in terms of electronic properties, and exhibit quantum dots and wires at very low temperature. However, SW-CNTs based sensing material was difficult to realize CNT-integrated devices.

This letter reports experimental results that demonstrate the pH sensing capability of MW-CNTs. High-density, well-aligned carbon nanotubes, which are MW-CNTs and vertically aligned on a large area of substrate, has been synthesized. A MEMS-based fabrication processes can be effectively applied to yield a single device or thousands of device. Key advantage of MEMS fabricated pH sensors include small device size and suitable device.

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Experimental

The pH sensor structure is shown in figure 1. A silicon wafer was oxidized to grow a 150nm thick SiO_2 insulation layer and lithography was used to create catalyst metal (cobalt, 8nm) for growth of MW-CNT film with a pair of electrodes pattern. The MW-CNTs film was deposited by thermal chemical vapor deposition.

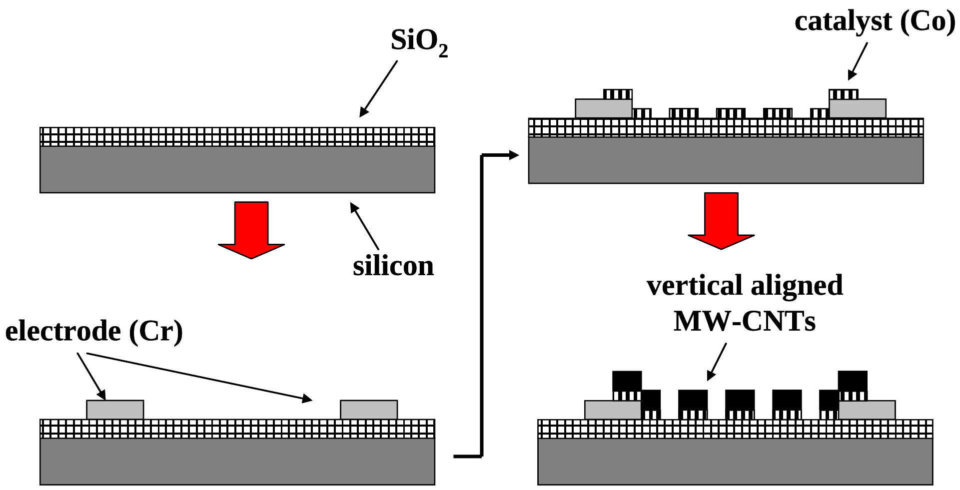

Figure 1. Fabrication process of MW-CNT pH sensor

This MW-CNTs pattern shown in figure 2 is the mesh type that well designed to react upon pH solution value. The MW-CNTs were grown by the pyrolysis of cobalt(Co) and acetylene(C_2H_2) gas under an argon (Ar)/hydrogen(H_2) atmosphere. The temperature of the thermal CVD chamber was raised to the process temperature of the 750℃ within 10-20 min by the halogen lamps after evacuation down to 10^{-3} torr.

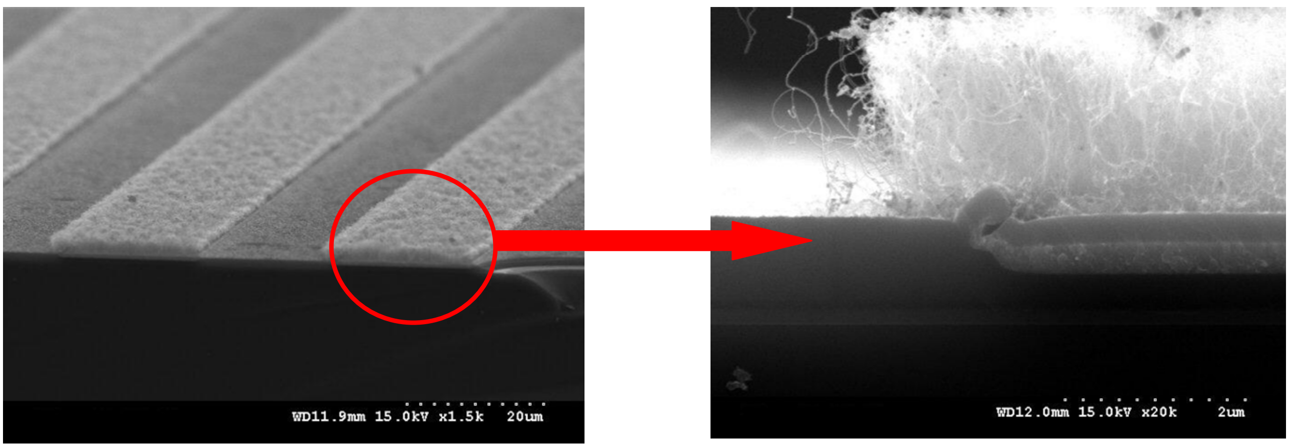

Figure 2. A FE-SEM of the mesh patterned MW-CNTs. It is designed to expand the reaction area.

We observed *in situ* measurement of electrical conductivity by cycling solution range from acid to base at room temperature. While pH solution value changed from acid to base, we rinsed the MW-CNTs using deionize(DI) water. The rinse activated the desorptive process that results in fast recovery from the MW-CNTs. To describe the pH response of the vertical grown MW-CNTs, 40mL of pH buffer solution was used. The conductivity of the MW-CNTs was measured using Keithley (Kithley Instruments, Inc., 4200SCS) at room temperature.

3. Results and Discussion

We experimentally found that the conductivity of the MW-CNTs was depended on pH range. Figure 3 shows the conductivity change of the MW-CNTs in pH buffer solution at pH 4, pH 7 and pH 10. It can be seen from figure 3 that conductivity(slope) of MW-CNTs increase with higher pH value. The conductivity change is due to the presence of semiconducting MW-CNTs dispersed among the predominant metallic MW-CNTs because MW-CNTs grown by CVD are not generally a single character of metallic or semiconducting but include both types. In almost cases, they show typical properties of metallic MW-CNTs. pH sensing characterizations of an MW-CNTs showing p-type semiconducting property were carried out.

pH dependent properties of the MW-CNTs are from the interaction between OH^- in pH buffer solution with semiconducting MW-CNTs. *Ab initio* study of this interaction confirm band-gap reduction of semiconducting MW-CNTs up on addition of the OH^- group. An additional energy level emerges near the Fermi level, which is due to coupling between one *p* orbital of the oxygen with the big π-bond of the MW-CNTs[6].

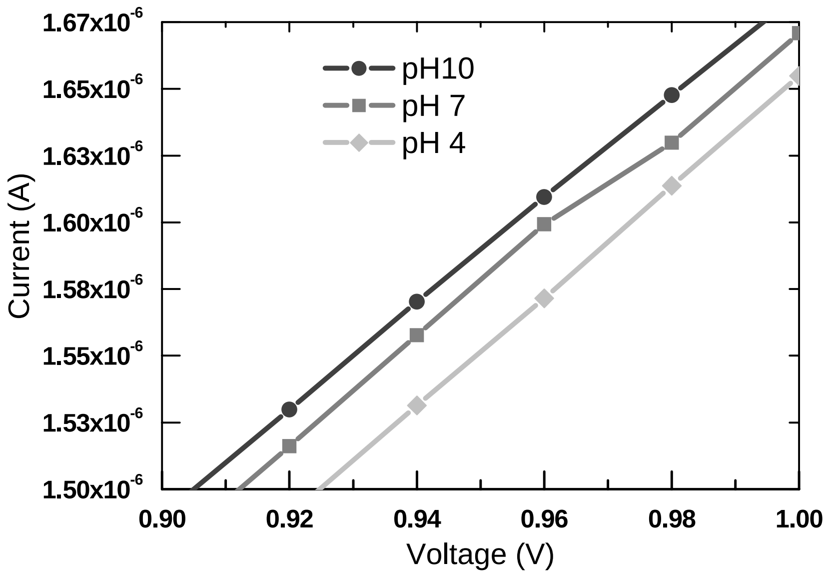

Figure 3. Current vs. voltage characteristics of MEMS-based MW-CNTs pH sensor.

3. Conclusion

In this paper, A MW-CNTs based on pH sensor was fabricated with MEMS fabrication. The electrical conductivity of the MW-CNTs were affected by different pH range environments. It was found that the conductivity of the MW-CNTs increase in response to higher pH range. The conductivity change is due to the presence of semiconducting MW-CNTs dispersed among the predominant metallic MW-CNTs. pH dependent properties of the MW-CNTs are from the interaction between OH^- in pH buffer solution with semiconducting MW-CNTs. The MW-CNTs based on pH sensor has been realized by MEMS-based fabrication.

Acknowledgement

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