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pH sensitive multiwalled carbon nanotubes

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Abstract

The CNTs-based sensors have received considerable attention because of their outstanding properties, such as faster response, higher sensitivity, and lower operating temperature. And we expect that CNTs-based electrochemical sensors offer substantial improvements in the performance of pH sensing device. This letter reports experimental results that demonstrate the pH sensing capability of the multiwalled carbon nanotubes (MWCNTs) film by using the thermal chemical vapor deposition (thermal CVD). It was found that electronic properties of MWCNTs can be changed by the introduction of different pH value solutions. The absorption of the hydroxide in pH buffer solution changes conductivity of the MWCNTs. We observed in situ measurement of electrical conductivity by cycling solution range from acid to base.

Keywords: Carbon nanotube; Sensor; Chemical vapor deposition

1. Introduction

Carbon nanotubes (CNTs) have a large surface-to-volume ratio and aspect ratio with the diameter of a few nanometers and length up 100 μm 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 is great interest in using CNTs as nanoscale probes and sensor in biological electronics devices because the chemical and physical properties of CNTs are extremely sensitive to the surrounding environments. The unique chemical and physical properties of CNTs have paved the way to new and improved sensing devices [1,2]. One main application of the CNT is for gas sensors [3–6]. We expect that CNTs-based electrochemical sensors offer substantial improvements in the performance of pH sensing device. The measurement of pH in solution is one of the most common tasks required in clinical analysis, environmental analysis and process control. Theoretical studies have predicted significant changes in the electronic properties of CNTs because of the hydroxide (OH) in pH solution. These results lead to the application of CNT as pH sensors. In other previous reports related to this issue, pH sensitive property of CNTs has been focused either on isolated singlewalled carbon nanotubes (SWCNTs) or on SWCNT mats [5,6]. The SWCNT is a well-defined system in terms of electronic properties, and exhibits quantum dots and wires at very low temperature. However, the isolated SWCNTs or SWCNT mats based sensing material was difficult to realize CNT-integrated devices.

This letter reports experimental results that demonstrate the pH sensitive capability of the Multiwalled carbon nanotubes (MWCNTs) film by thermal chemical vapor deposition (CVD) method. The MWCNTs film by the thermal CVD method is easiest to scale up to industrial production, long length, simple process and the MWCNTs film pattern as mesh type was designed to expand the reaction area.

2. Experiments

The pH sensor structure is shown in Fig. 1. This sensor was 1.5×1.5 mm^2 and 450 μm thick. And the MWCNTs film area was 1×1 mm^2. A silicon wafer was oxidized to grow a 150 nm

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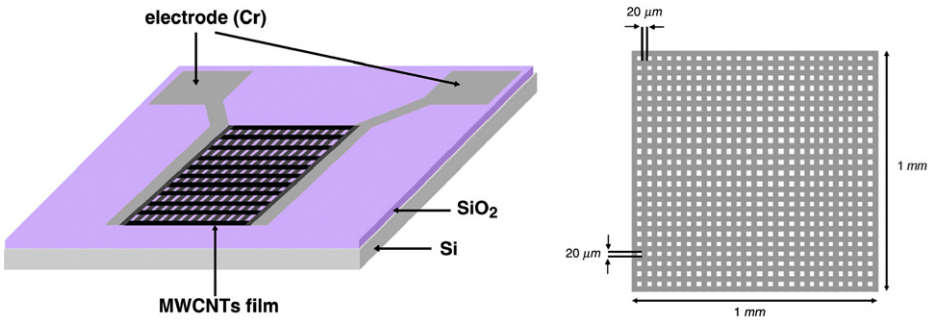

Fig. 1. Schematic of the MWCNT pH sensor (a) and MWCNT film pattern (b).

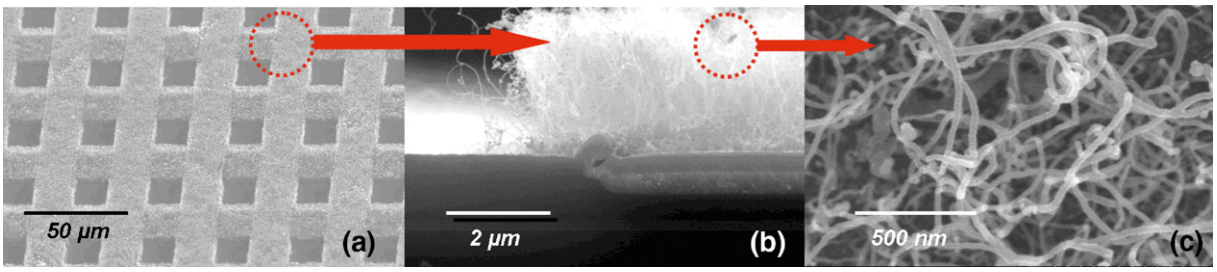

Fig. 2. A FE-SEM of the mesh patterned MWCNTs. It is designed to expand the reaction area.

thick SiO_2 insulation layer and lithography was used to create catalyst metal (cobalt, 8 nm) for growth of MWCNTs film with a pair of electrodes pattern. The MWCNTs were grown by thermal CVD method. The thermal CVD method to synthesize the MWCNTs used in this work has been reported earlier [7]. The MWCNTs film pattern shown in Fig. 2 is the mesh type that is well designed to react upon the pH solution value.

The MWCNTs 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 750 °C within 10–20 min by halogen lamps after evacuation down to 10^{-3} Torr. During this step, the substrate was firstly treated under a hydrogen (H_2) gas environment for nearly 10 min to activate the surface of the catalytic metal and to prevent the corrosion of the catalytic metal and Cr electrode metal due to the residual gases. During growth, the total pressure of the chamber was constantly kept at 20 Torr and the flow rate of the hydrocarbon source, C_2H_2, was 5 sccm and that of ammonia (NH_3) was 80 sccm. After the MWCNT growth, the chamber was purged continuously with a mixture of H_2 and Ar until the chamber temperature reached room temperature. Fig. 2(b) and (c) shows the FE-SEM of the well aligned vertical grown MWCNTs by thermal CVD method. The mesh film system increases the side surface area of the MWCNT with the dominant tube length ≈ 5 μm. We observed in situ measurement of electrical conductivity by cycling solution range from acid (pH 4) to base (pH 10). The conductivity of the MWCNTs was measured by using Keithley (Keithley Instruments, Inc., 4200SCS) at room temperature. To describe the pH response of the vertically grown MWCNTs, 0.5 μL of pH buffer solution is placed on top of the MWCNTs film based sensing area.

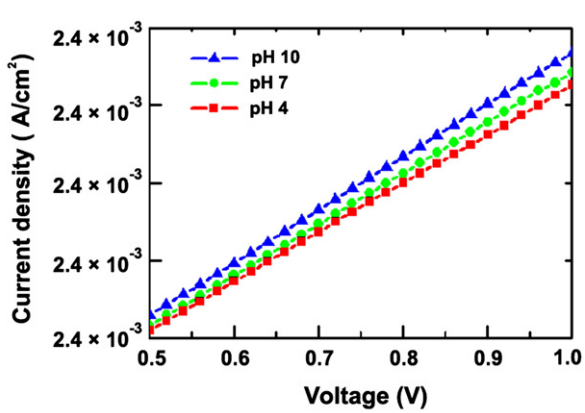

Fig. 3. Current density vs. voltage characteristics of MWCNTs with the pH buffer solution at pH 4, pH 7 and pH 10.

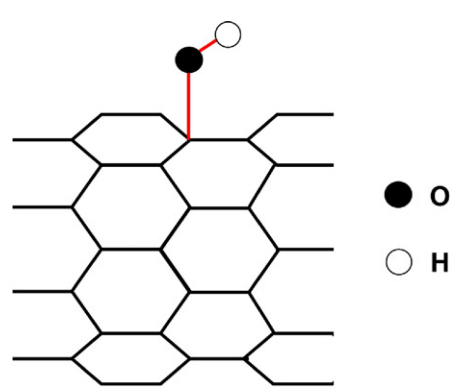

Fig. 4. Side views of the hydroxide molecule attached to the CNT.

3. Result and discussion

We experimentally found that the conductivity of the MWCNTs depended on the pH range. Fig. 3 shows the conductivity changes of the MWCNTs in pH buffer solution at pH 4 (acid solution), pH 7 (neutrality solution) and pH 10 (base solution). It can be seen from Fig. 4 that conductivity ($\Delta I/\Delta V$, slope) of the MWCNTs film increases with a higher pH value. Adding a base (pH 10) to water increases the hydroxide ion concentration and decreases the hydronium ion concentration. Adding an acid (pH 4) does the opposite. The pH is defined mathematically as the negative logarithm of the hydronium concentration and the pOH is also defined a complementary scale for the hydroxide concentration. Strictly speaking, we measured the pOH, not the pH. But the pH and pOH of a water solution at 25 °C are related by pH + pOH = 14. Therefore, if either the pH or the pOH of a solution is known, the other can be quickly calculated.

Theoretical studies have predicted significant changes in the electronic properties of MWCNTs because of the interaction between the hydroxide in the pH solution and the surface of the MWCNTs (Fig. 4). So, we fabricated the MWCNTs pattern as mesh type that was designed to expand the reaction area. Due to the OH group that was attached on the wall of the MWCNTs, the pH buffer solutions can increase or decrease the conductivity of the MWCNTs depending on whether the solution is an acid or base. The small conductivity change is due to the presence of semiconducting MWCNTs dispersed among the predominant metallic MWCNTs because MWCNTs grown by CVD are not generally a single character of metallic or semiconducting but include both types. In most cases, they show typical properties of metallic MWCNTs. OH sensing characterization of MWCNTs showing p-type semiconducting properties was carried out. It is well known that the three p orbitals of oxygen in hydroxide group are perpendicular to each other. The bond of the sp hybridization is formed by one p orbital (p_z) of oxygen and the s orbital of hydrogen is roughly perpendicular to the C–O bond because another p orbital (p_x) of oxygen forms a bond with one p orbital of carbon. It can be concluded that the local sp^2 hybridization was destroyed due to the introduction of the hydroxide group, and the C–C bond becomes longer than that in pure CNT. This distortion and the addition of the hydroxide group lead to the differences in the electronic properties of the CNT–OH system and pure CNT. The pH value dependent properties of the MWCNTs are from the interaction between the hydroxide group in the pH buffer solution with MWCNTs. *Ab initio* study of this interaction confirms band-gap reduction of semiconducting MWCNTs upon addition of the hydroxide group. An additional energy level emerges near the Fermi level, which is due to coupling between one p orbital of oxygen with the big π-bond of the semiconducting MWCNTs. Because when the hydroxide group is introduced to the tube wall, a peak in the dense of state (DOS) arises at the Fermi level and the energy gap is significantly reduced. Hydroxide group can form an acceptor level, and enhance the conductivity of the semiconducting MWCNTs. That is, the OH group can be a good acceptor for hole doping [8,9].

4. Conclusion

The pH sensor was successfully realized by thermal CVD growth of the MWCNTs sensing film. The MWCNTs film by the thermal CVD method is easiest to scale up to industrial production, long length, simple process and the MWCNTs film pattern as mesh type was designed to expand the reaction area. We observed in situ measurement of electrical conductivity by cycling solution range from acid (pH 4) to base (pH 10). The electrical conductivity of the MWCNTs was affected by different pH range environments. The pH dependent properties of the MWCNTs are from the interaction between hydroxide in the pH buffer solution and the surface of the semiconducting MWCNTs. So, we fabricated the MWCNTs pattern as mesh type that was designed to expand the reaction area. And we confirm that conductivity of the MWCNTs film increases with higher pH value. In other words, pH buffer solutions can increase or decrease the conductivity of the MWCNTs depending on whether the solution is an acid or base. These results show that our technique can be further optimized for increased sensitivity of aqueous-phase pH sensing.

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References

[1] H. Dai, et al., Accounts of Chemical Research 35 (2002) 10351.
[2] M. Meyyappan, Carbon Nanotubes: Science and Application, CRC Press, New York, 2005.
[3] Q. Zhao, et al., Electroanalysis 14 (2002) 1609.
[4] K. Ong, et al., IEEE Sensors Journal 2 (2002) 82.
[5] Z. Xu, et al., Biosensors and Bioelectronics 20 (2004) 579.
[6] W. Zhao, et al., Journal of the American Chemical Society 24 (2002) 12418.
[7] C. Lee, et al., Chemical Physics Letters 312 (1999) 461.
[8] H. Pang, et al., Physical Review Letters B 70 (2004) 245425.
[9] H. Chang, et al., Applied Physics Letters 79 (2001) 3863.