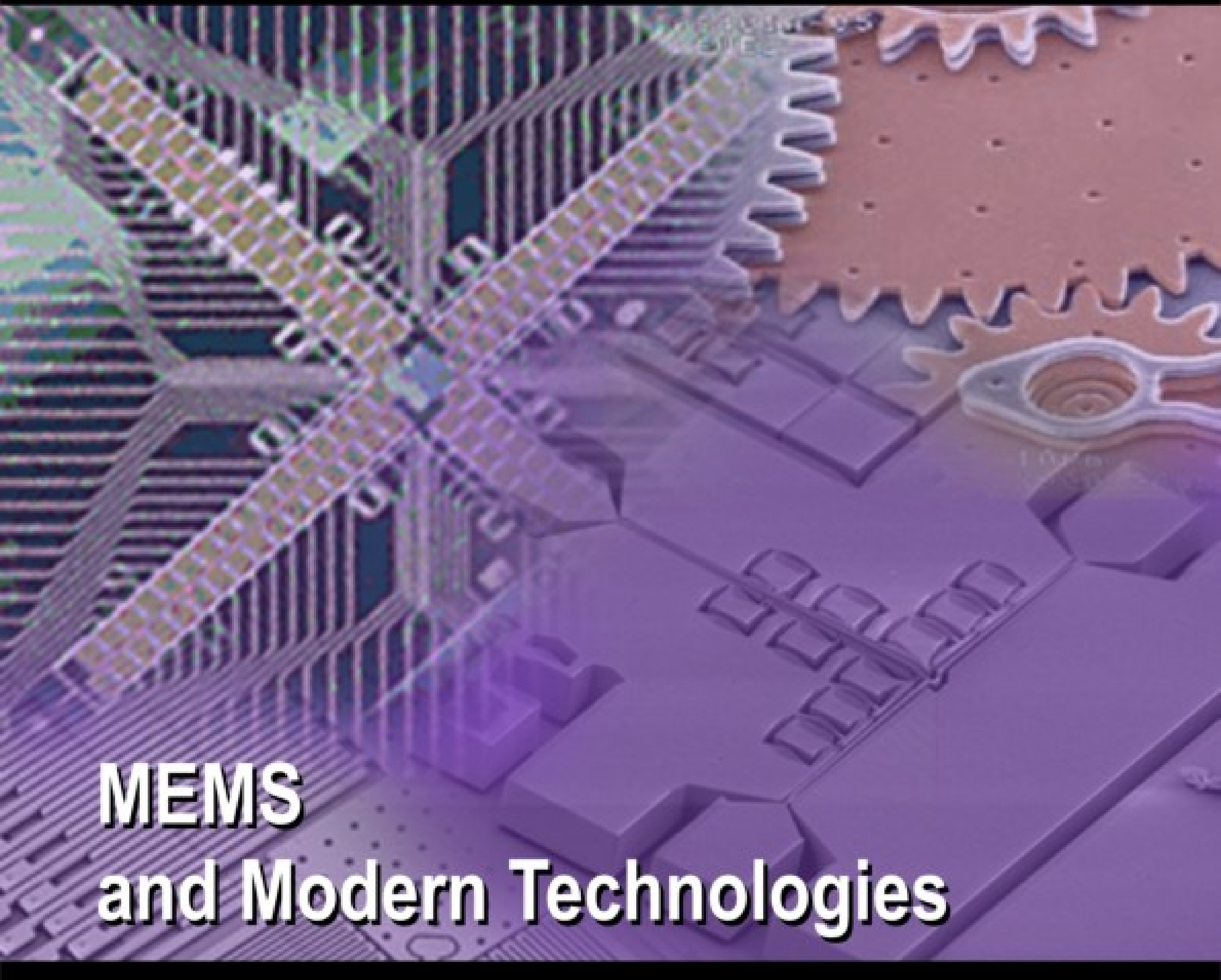
ISSN 1726-5749

SENSORS & TRANSDUCERS

vol. 91
4/08



MEMS and Modern Technologies

International Frequency Sensor Association Publishing

IFSA

Sensors & Transducers

Volume 91
Issue 4
April 2008

www.sensorsportal.com

ISSN 1726-5479

Sensors & Transducers Journal (ISSN 1726-5479) is a peer review international journal published monthly online by International Frequency Sensor Association (IFSA).
Available in electronic and CD-ROM.

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Volume 91
Issue 4
April 2008

www.sensorsportal.com

ISSN 1726-5479

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Sensors & Transducers

ISSN 1726-5479

http://www.sensorsportal.com

A Sensor for Gas Detection Fabricated by a Circular Single-wall Carbon Nanotube

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Received: 8 April 2008 /Accepted: 23 April 2008 /Published: 30 April 2008

Abstract: This work endeavors to describe a circular shape of carbon nanotubes (CNT) performed by ultrasonic agitation and assisted by a surfactant implemented for gas detection. In a well-dispersed CNT solution, we observed that the thinner thickness and the larger diameter CNT rings were formed than those of our previous study. This fact can be elucidated more fully that the depletion contact energy is modulated by theoretical estimation with the corresponding tendency in our samples. The separated CNT ring possessed with negative charges in sodium dodecyl sulfate (SDS) surfactant solution can be easily absorbed on the sliced surface. Through the e-beam lithography and the lift-off process, a CNT ring was exploited as a gas sensor to detect an extremely low concentration of methane gas. The circular CNT sensor has a prominent conduction response embodied in the existence of more defects in the ring CNT sensor than those of the straight CNT sensor. Moreover, the much fast response time in the circular CNT illustrates the demand of the shorter length of CNTs. The CNT ring features with longer persistent to current conduction after long time measurements appraising to be a robust and durable material in the sensor applications. *Copyright © 2008 IFSA.*

Keywords: Circular carbon-nanotubes, Gas sensors, Ultrasonic agitation, Dodecyl sulfate surfactant

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1. Introduction

Carbon nanotubes (CNTs) featured with fascinating properties in high mechanical strength, persistent to chemical erosion [1], high electron field emission characteristics [2], and the unique one-dimensional electrical transport [3] properties are largely exploited in the detection of organic gases

[4]. Gas and solvent molecules can react with the surface molecules of CNTs surrounded with π electrons. Therefore, sensor devices composed of CNTs were widely studied by many researches and fabricated by several techniques such as dielectrophoresis [5], and directly growth method [6, 7, 8]. The conspicuous performance of the CNT sensor provides us to detect low level of organic gas. Up to now, the mechanism of the CNT sensor is not quite clear and is extensively recognized that more active sites including defects, large diameter and opened tip will enhance the sensitivity of the CNT sensor. As a result, CNTs powder has to be purified in order to increase the active sites to adsorb gases before to be fabricated as a gas sensor. Generally, the morphology of the CNT gas sensors have been illustrated as mats of CNTs [9, 10], a well-aligned CNT array [7, 8] or an individual CNT [11].

In this paper, the synthesized straight CNTs were manufactured into circular structure in processes of purification, than by surfactant immersion and ultrasonic agitation. The formation of the circular shape was addressed by a continuum shell model. Nevertheless, the circular shape of CNT sensors has not been illustrated yet. We found that the circular CNTs are much more sensitive than the straight ones with conceivable active sites formed on the curved CNT surface. Consequently, much favors ensuing on this study provide a much higher sensitivity and persistent in CNT sensors.

2. Experimental Procedures

In this work, the SWCNT powder was firstly immersed in the nitric acid for 24 hours and then mixed with distilled water and SDS (sodium dodecyl sulfate) surfactant. When the SDS concentration is slightly above the critical micelle concentration (CMC), a well suspension of water-nanotubes can be obtained [12]. The CNTs were mixed with SDS at a concentration of 4 CMC and then the tangled SWCNTs could be separated into well-dispersed individual SWCNT by ultrasonic agitation for 9 hours. The surface of CNTs surrounded by SDS molecules possesses negative charges. On the other hand, we implemented the heavily doped silicon substrate for high conduction which is insulated by a thermally grown SiO_2 on the top surface with a thickness of 400 nm. The substrate was transferred into the oxygen plasma system for 15 minutes to produce hydroxyl groups on the surface, which was then modified by reacting with 3-aminopropyltriethoxysilane (APTMS) to the molecular ends by the ammonium groups with positive charges. Several droplets of well-dispersed CNTs solution were dropped on the functionalize surface for 5 minutes and the CNTs attached with negative charges were attracted on the modified surface by electrostatic interactions. After the substrate was rinsed intensively with the distilled water and to be blown with N2 to dry, the excess micelle surfactant absorbed on the CNT surface should be removed by washing in distilled water. The overall process is schematically shown in Fig. 1.

The circular CNTs were connected to the external gold electrode by the lift-off process as shown in Fig. 3. In order to form an ohmic contact between the metal electrodes and the CNT, we deposited a thin titanium film as the adhesion layer which was then covered by a gold film. After making the internal wire connection, the sample was loaded into the gas detection system to measure the resistivity changes due to the fill and evacuation of the desired sensing of the gas exploiting by a Keithley 2410 meter.

3. Results and Discussion

Circular structure of carbon nanotubes have been firstly discovered by Liu et al. [13] during an inspection of CNTs grown by laser ablation. They found a trace of toroidal remnant in the CNT powder revealing a lot of perfect structure. The toroidal CNTs without showing the terminals were formed by the carbon-to-carbon covalent bonds during the growing process. Additionally, other investigators revealed that the circular structure can be manufactured by ultrasonic agitation in an organic solvent [14]. The circular CNTs, however, had a distinct formation mechanism portrayed by Liu's group. These CNT rings have some artificial integration through many steps specifying the fact that the total energy including strain energy and cohesive energy determines the possibility to form the circular CNTs. The critical radius of several types of CNTs has no correlation between the diameter of the rings and their thicknesses. When the CNT assembles to form a circular shape via ultrasonic agitation in an organic solvent, the large activation energy EA for the ring formation is thermally dynamically justified by the energy dependence on R as $E_A \propto \frac{1}{R^2}$. Consequently, the diameter of CNTs may be ranged from 300-400 nm with wall thicknesses lying between 10-20 nm as indicated in previous reports.

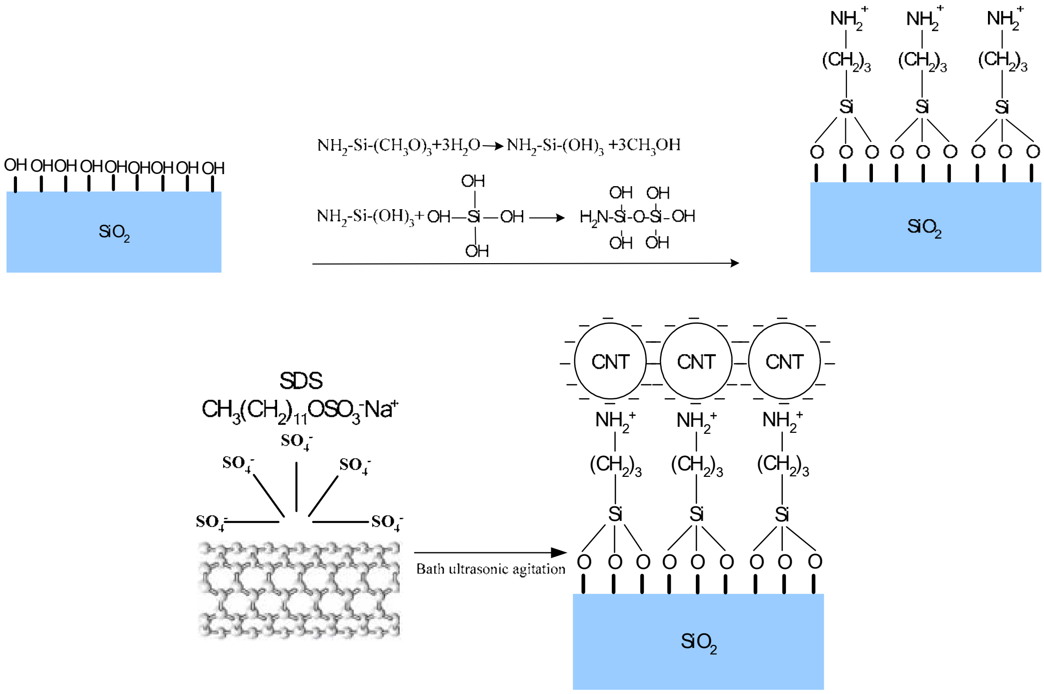

Fig. 1. Schematic representation of SWCNTs surrounded by negative charges of surfactant shell being moved onto the amino-silanized SiO_2 surface.

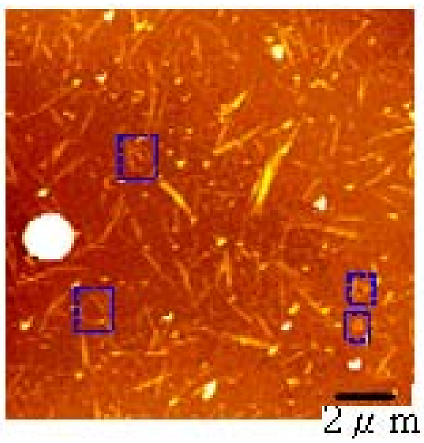

Fig. 2. The plate shows an AFM image where many CNTs were densely dispersed on the substrate surface. Additionally, the circular CNTs with different diameters are indicated by the blue squares as sketched on the surface.

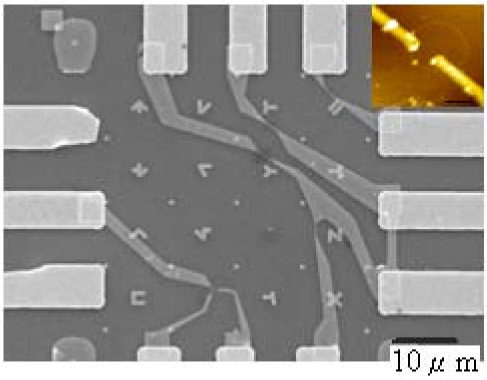

Fig. 3. The SEM image of the inter-connectors with showing 12 metal electrodes. The inset of the AFM image shows the connection between the circular CNT ring and two metal leads with a. scale bar of 0.5 μm.

In this study, we observed that the circular CNTs as shown in Fig. 1 have a radius within the range of 0.5~1.5 μm with wall thicknesses between 2~8 nm. The circular CNTs of our samples, however, inherit with a larger diameter and thinner thickness than other researches. The forming mechanism will be modified to address the speculated plausible diameters. Including the consideration of the strain and the cohesive energy, the formulas can be defined by the continuum shell model as sketched in eqs. (1) and (2) [15, 16, 17]. To elucidate a right perspective to the theoretical prediction to our experimental result, the formation mechanism of the circular CNTs should be reconsidered. Noting the condition in our investigation that the CNTs suspension is stabilized in water with SDS at 4 CMC with adding SDS surfactant into water to obtain a stabilized CNTs suspension with flat surface, the result is shown in Fig. 4 to reveal the flocculation of two CNTs. If the distance d between two CNTs with SDS surfactant becomes smaller than the diameter of the micelles σ_1, the micelle represented as spheres would be ruled out the volume between two CNTs. Consequently, the concentration difference implies an osmotic pressure causing the attraction of these two CNTs [18]. Similarly, the formation of circular CNTs also has the same effect on the water-nanotubes suspension stabilized with SDS. When the bubbles produced under ultrasonic agitation come close to the nanotubes surface, the collapsed bubbles bend the nanotubes so that the end of nanotubes possibly connects to each other through the osmotic effect. The depletion contact energy between two cylindrical CNTs with diameter σ_2 and contact length L can be performed as indicated in eq. 3.

The SDS micelles in diluted solution can be considered as an ideal gas by which the osmotic pressure P can be represented as P=nKT where n is the SDS mole concentration, k is Boltzman constant and T is the temperature. The external energy for the linearly chained CNT to become a circular coil can be estimated. The smaller the CNT diameter, the larger the strain energy or the less of the cohesive energy can be predicted. The depletion contact energy, however, supplies additional energy to form the circular CNT. As sketched in Fig. 5 shows that the large diameter of CNTs can be easily formed with fewer contact segments with less assistance by the osmotic pressure. With the aid of the AFM image that the larger ring CNT of about micro-meter in size with thinner thickness can be readily formed in organic solvents. The images illustrates that the SDS micelle in fact not only separate the tangled carbon nanotubes into a well-dispersed solute but also help the inter-tangled individual nanotubes at the tube end to form the circular structure through ultrasonic agitation and osmotic effect. As a result, the circular CNTs in our sample expresses a fact that the thinner thickness implies a larger radius due to the aid with the osmotic effect. Mathematically,

$$\mathrm{E}_s = \frac{Y \cdot I}{2R^2} \times (2\pi \mathrm{R} + \ell) \tag{1}$$

$$\mathrm{E_C} = -K\ \ell \tag{2}$$

$$\mathrm{E}_c = -PL[\frac{\sigma_2}{2\sqrt{4\bar{\sigma}^2 - \sigma_2^2}} + 2\bar{\sigma}^2 \arcsin(\frac{\sigma_2}{2\bar{\sigma}})] \quad , \quad \bar{\sigma} = (\sigma_1 + \sigma_2)/2 \tag{3}$$

implies

$$\mathrm{E}_{total} = E_s + E_a + E_c \tag{4}$$

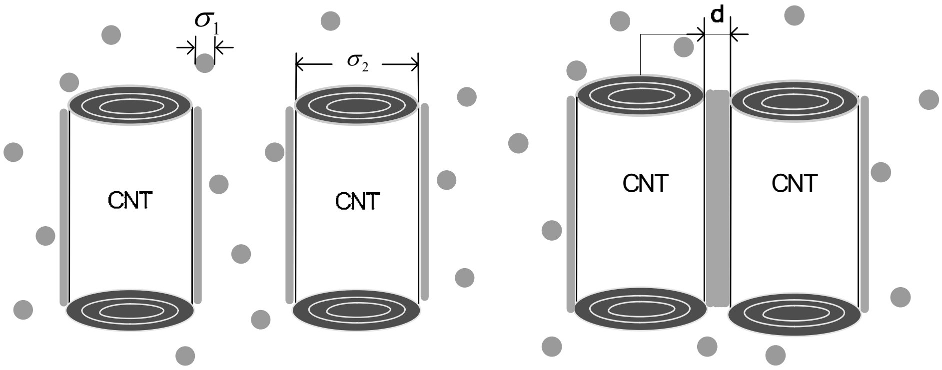

Fig. 4. The schematic diagram showing the flocculation process. The diameters of micelle are indicated by σ_1 and CNTs are indicated by σ_2.

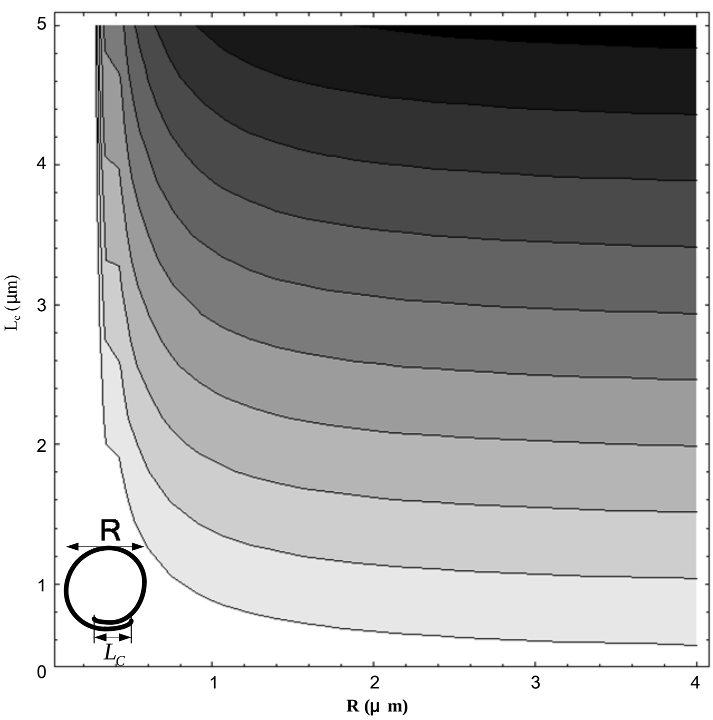

Fig. 5. The thermally dynamical analysis of the circular CNT, where the wall thickness is 0.066 nm and the diameter is 2 nm as described by the continuum shell model. The total energy including strain energy, cohesive energy and depletion contact energy is plotted in the gray area with the white to dark color to specify a range from 0 to -2500 eV.

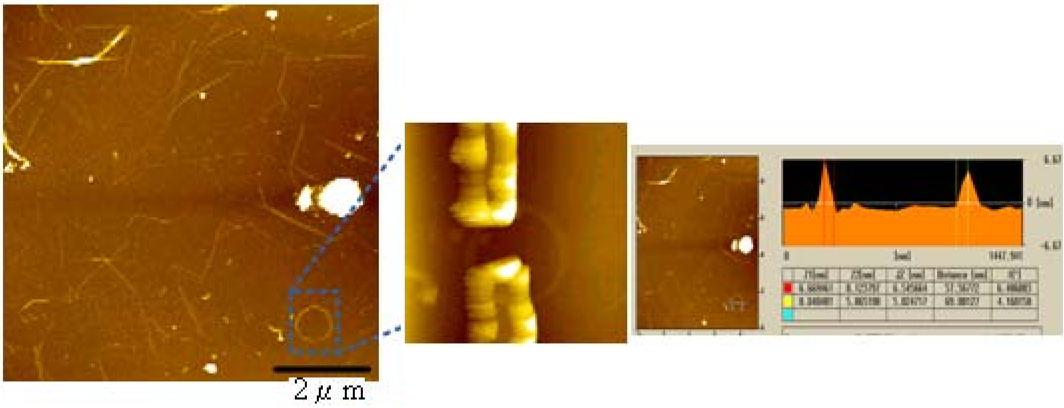

Fig. 6. AFM image of CNTs ring with the diameter of 893 nm and the thickness of 5~6 nm were connected by two gold leads through e-beam lithography and lift-off process.

After the AFM inspection of the wire connectors, the circular CNT was then covered with titanium and gold films which were implemented as the internal connector as shown in Fig. 6. To reduce the contact resistance, titanium film was used as the adhesion layer. The surfactant was washed out by distilled water for 30 minutes because the SDS micelle attached to the CNT surface could affect the accuracy of the gas detection. The detection of 1ppm methane gas reveals that the circular CNT sensor has much remarkable response. The resistance variation of that sensor can be up to 21.38 % with a response time of 65 seconds as shown in Fig. 7. Comparing to our previous sample as shown in Fig.8 for the straight SWCNT sensor with the performance as sketched in the Fig. 9 reveals that the resistance changes 1.23 % with the response time of 149 seconds during gas sensing [4]. The plausible reason for explaining the enhancement of resistance variation is that the bended circular CNT inherits with much more defect sites than the straight SWCNT. Sophisticatedly, the curved CNT ring is not a perfect pentagon-heptagon pairs but the damages formed by the bubble collapse on the nanotube surface to produce more defects sites during the coiling process. On the other hand, the response time in circular CNT sensor is shorter than that in the straight CNT sensor. The fast response in the CNT ring may imply that gas sensing with less nanotubes that can quickly detect the reaction between the methane gas and the nanotube surface.

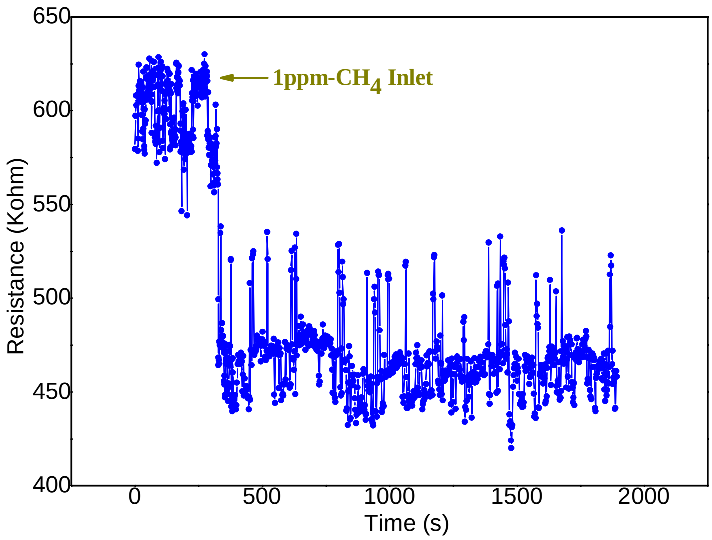

Fig. 7. Resistance response of the circular SWCNTs upon exposure to 1ppm CH4.

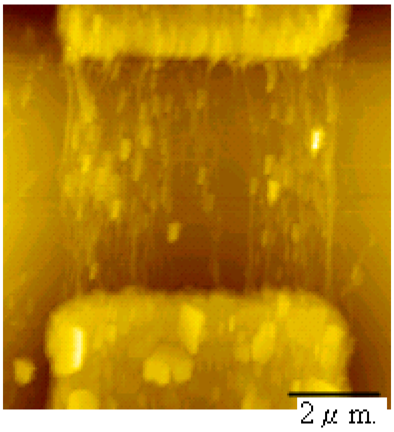

Fig. 8. The AFM image of the straight SWCNTs was fabricated by DEP.

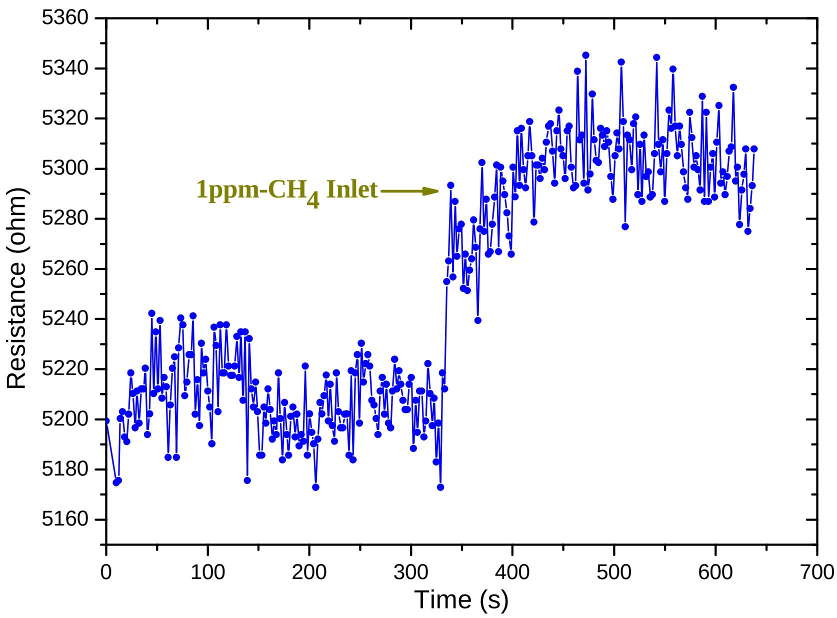

Fig. 9. The resistance response of the straight SWCNTs upon an exposure to 1ppm CH4.

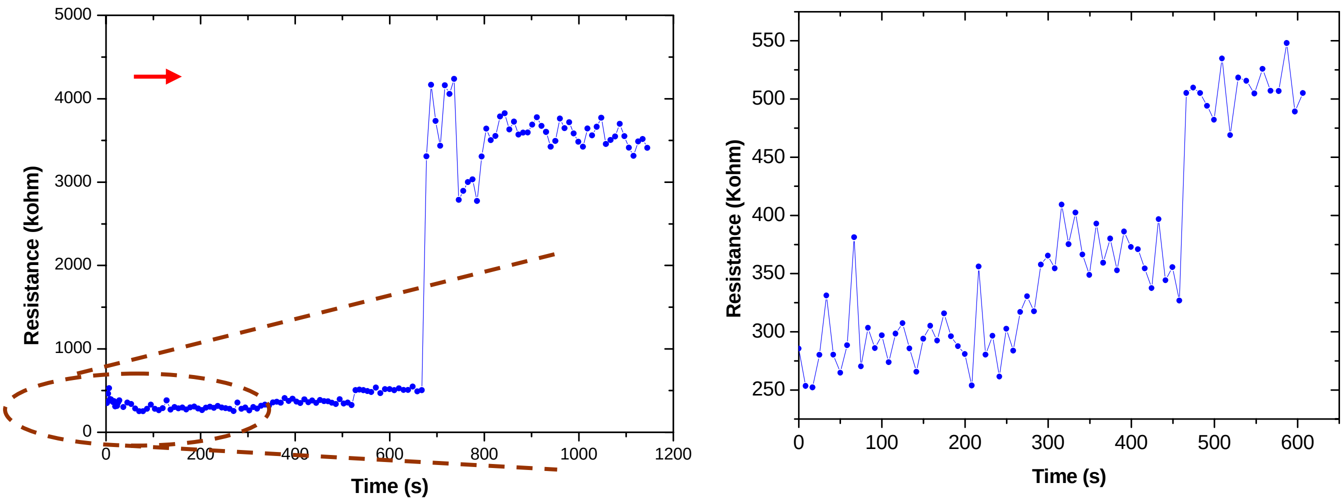

Fig. 10. The resistance response of a circular CNT sensor during long time measurements. The red arrow indicates the electrical breakdown of the sensor.

After detecting the methane gas, the durable capability of circular CNT sensor was tested as shown in Fig.10. A small current about 50 nA continued to flow through the sensor device. The current density can be up to 1.7×10^{8} (mA/cm^2). The inset reveals that the resistance staircase can be increased from ~293 kΩ (or 373 kΩ) to 512 kΩ. The result indicates that electron current flow may enlarge the defects area so that the resistance of the CNT ring gradually increases. After 10 minutes later, the resistance breakdown of circular shape CNT sensor occurs and the resistance sharply increases from 512 kΩ to 3.5 MΩ. Fig. 11 shows that the circular CNT is not broken but a gold lead is melted under such a high current flow. The result appears that the CNT ring is robust for a high current flow. If the contact metal is persistent to endure high current flow, the circular CNT sensor might be the much germane choice for a gas sensor.

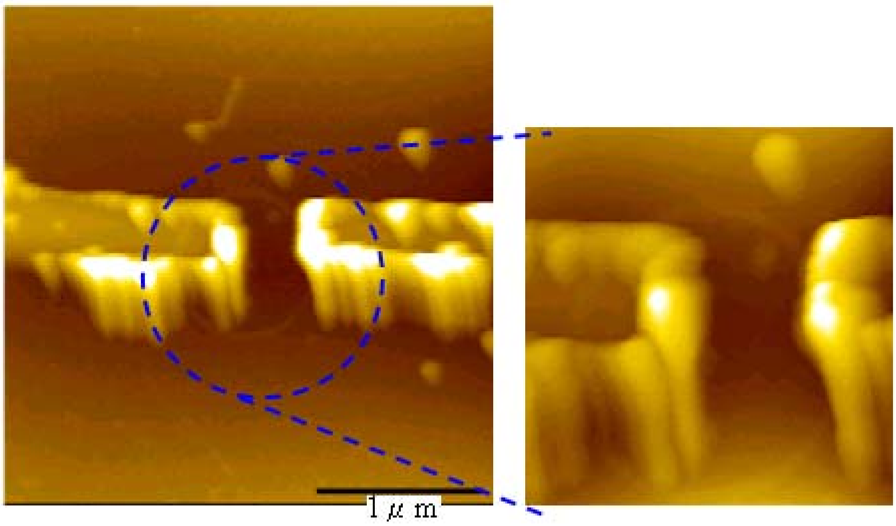

Fig. 11. AFM image of a circular CNTs sensor after long time measurement.

4. Conclusions

We have successfully fabricated from the integration of straight SWCNTs into a circular CNT sensor through ultrasonic agitation of the CNT powder with SDS surfactant in water-nanotube suspension. The achievable CNT rings have larger diameters and thinner thicknesses than other works. Based on the experimental results observed in our sample, we modulated the applied electrical bias during the coiling process. The depletion contact energy has to be taken into account in the colloidal solution and therefore we can found a larger diameter ring in our CNTs solution than before. On the other hand, we utilized the circular CNTs as a sensor to detect the methane gas. The change of resistivity variation and response time are much more sensitive and fast in the CNT ring sensor than those in the straight one. It implicates that more defects existed in bend CNTs than those in straight ones ensuing enhancement in capturing invade molecules for gas sensing. The mechanical and electrical superiors of CNTs [19] appraise the CNTs for pragmatic uses in gas sensing. The age testing with continuous current flow, suggesting that the CNT ring sensor has a much durable capability in gas detection.

Acknowledgements

The authors are indebted to the National Science Foundation of the Republic of China for the support of the project NSC 97-2112-M007-.

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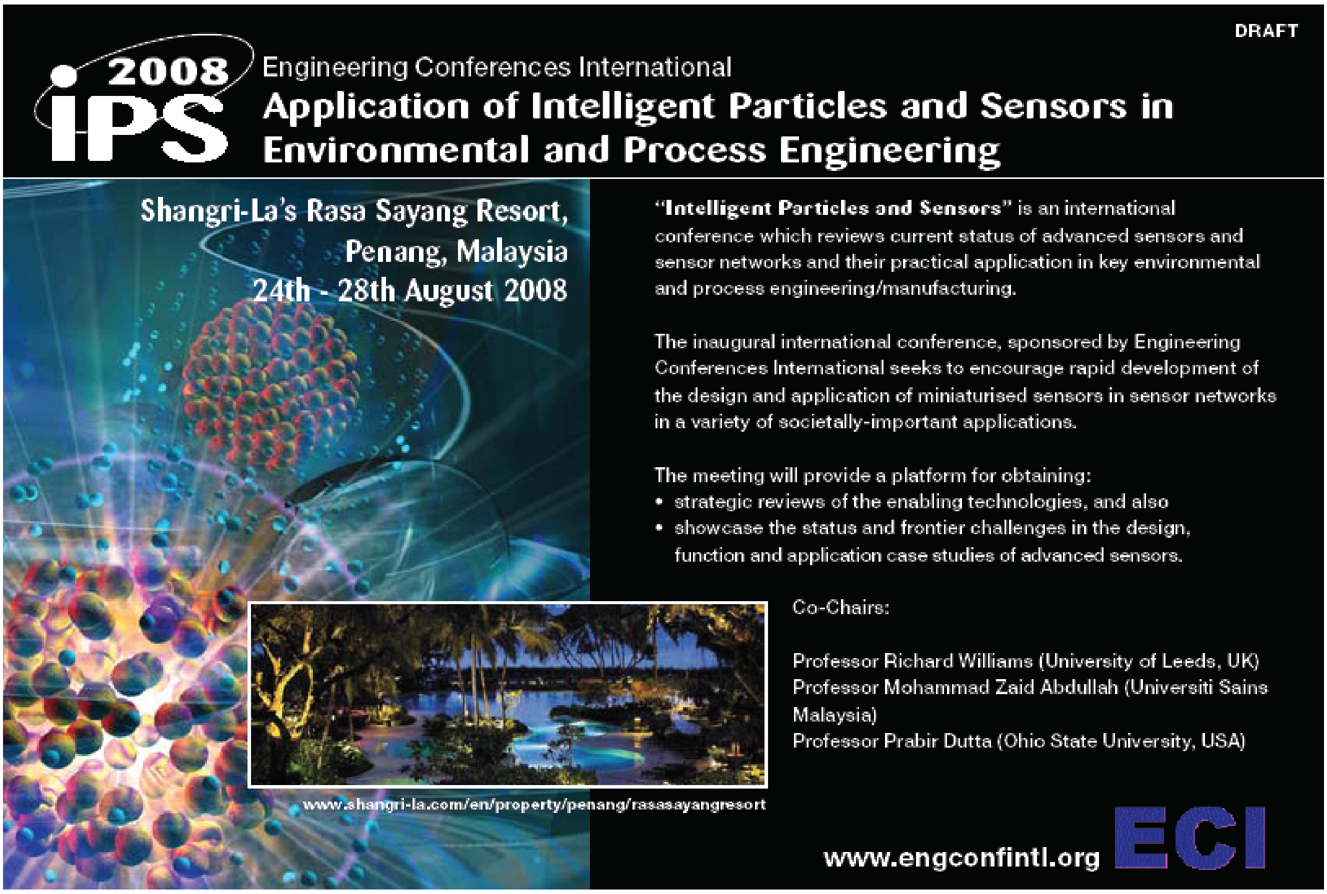

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