Proceedings of the 3rd IEEE Int. Conf. on
Nano/Micro Engineered and Molecular Systems
January 6-9, 2008, Sanya, China

Constant-Power Operation of Functionalized Carbon Nanotube Sensors for Alcohol Vapor Detection

Mengxing Ouyang[1], Mandy L.Y. Sin[1], Brittle K. H. Tsoi[2], Gary C.T. Chow[2], Gary M.K. Wong[3], Wen J. Li[1,*], *Member, IEEE, Member, ASME,* Philip H.W. Leong[2], *Senior Member, IEEE,* and Ka Wai Wong[3]

[1] *Centre for Micro and Nano Systems, Department of Mechanical and Automation Engineering*
[2] *Department of Computer Science and Engineering*
[3] *Department of Physics*
The Chinese University of Hong Kong, Shatin, N.T., Hong Kong SAR, China

***Abstract* — A constant-power control circuit has been built successfully for the digital operation of CNT-based alcohol vapor sensors. The sensors, which are based on bundles of chemically functionalized multi-walled carbon nanotubes (f-CNTs), have been proven to be sensitive towards alcohol molecules. The resistance of the sensors increases upon exposure to alcohol vapors. The constant-power configuration is developed to avoid the self-heating effect, which is a significant factor in affecting the sensor performance. On the other hand, we also utilized the self-heating effect to clean up the alcohol molecules on the f-CNTs between measurements. The comparison experiments between constant-power and constant-current configurations were conducted. The results demonstrated larger response under constant-power mode, especially when operating power was low or alcohol concentration was relatively high. The responsivity and the sensitivity of alcohol vapor sensors under different mode and operating powers are also discussed.**

Keywords — **CNT functionalization, chemical sensors, constant-power configuration, alcohol vapor detection, and CNT sensors.**

I. Introduction

With merits of minute size of the sensing element and the correspondingly small amount of material required for a response [1], carbon nanotube sensors have been receiving considerable attention. Exhibiting high aspect ratio [2], the capability of carbon nanotubes to serve as chemical sensing elements has been proved [3, 4]. Over the last decade, many research groups have been focusing on the gas adsorption mechanism of carbon nanotubes [5-8] as well as utilizing carbon nanotube based sensors to detect gases, such as CO_2 [9], NO_2 [10], and ammonia gas [11], etc. Among all these applications, alcohol vapor has always been one of the most extensively studied species due to the demand of small practical devices to detect alcohol for breathalyzer or to identify industrial leakage in distribution lines [12].

Our group has been studying CNTs based alcohol vapor sensor since 2006 [13]. In our previous work, carbon nanotubes grafted with several kinds of functional groups have been proved sensitive towards ethanol molecules, and their potential to serve as alcohol vapor sensor have been demonstrated. The functional groups not only can enhance the sensibility of the alcohol vapor sensor, but also enable CNT sensors to achieve better selectivity towards different variables. In addition, we also evaluated different functional groups through both chemical and physical functionalization methods for the purpose of optimistic sensor performance. In this paper, we will present our latest progress on the alcohol vapor sensors based on f-CNTs with COOH group fabricated by chemical oxidation. The sensor characterization and its response under different operating power units will be discussed. In addition, sensor performance towards both constant-current and constant-power configurations will be evaluated. Moreover, we will also discuss the sensor responsivity and sensitivity under different operating power as well as different configurations.

II. Fabrication and Characterization of the f-CNTs Based Alcohol Vapor Sensor

A. Fabrication of f-CNTs Based Alcohol Sensor

In our experiments, commercially available multi-walled carbon nanotubes (MWNTs) were employed and chemical oxidation method was used to graft functional group (e.g., –COOH) along the sidewall and the tube ends of the carbon nanotubes (see Fig. 1). After purification, sonication, and centrifugation, the functionalized MWNTs were collected, washed, and re-dispersed in solvent for use. The detail of functionalization process of carbon nanotubes are presented in [14].

Dielectrophoresis (DEP) manipulation was used to form carbon nanotube linkage between microelectrodes [15], which were fabricated on Si substrate by photolithography procedure. During the formation, a droplet of f-CNTs solution was transferred to the gap between a pair of Au microelectrodes, which were excited by AC bias voltage. After a while, solvent evaporated, leaving f-CNTs connection between the two tips. Typically, the two-probe room temperature resistance of the f-CNTs based devices range from several tens of kilo ohms to

This project is funded by the Hong Kong Research Grants Council (Project code: 413906) and by the Hong Kong Innovation and Technology Commission (Project code: ITS/027/06).
Contact author: **wen@mae.cuhk.edu.hk.*

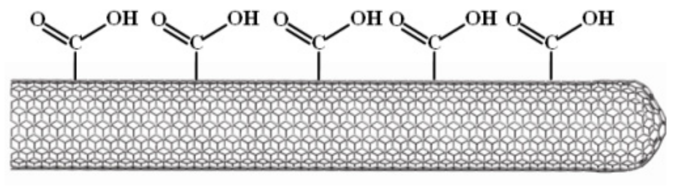

Figure 1. Chemically functionalized CNTs with COOH group attached on the sidewall.

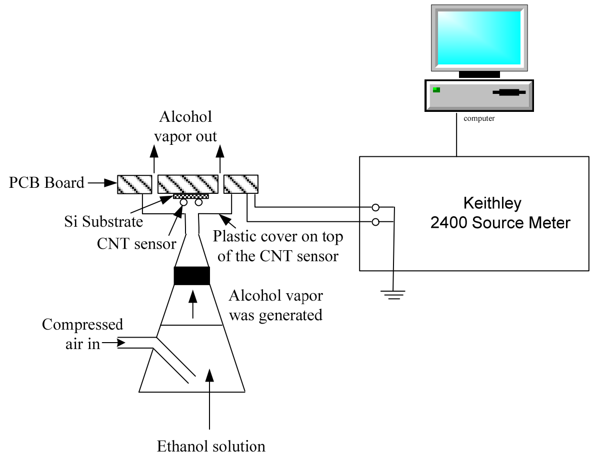

Figure 2. Experimental setup of alcohol vapor sensor under constant-current mode.

several hundreds of kilo ohms depending on the concentration and volume of the solution droplet. For the purpose of electrically connection with the measuring unit, the sensor chip was then fixed and wire-bonded to a printed circuit board (PCB) board, where several small holes were drilled for the outlet of alcohol vapor. And then, a plastic cover was put on top of the sensor chip. During the experiments, the alcohol vapor as generated by directing a well-controlled flow of compressed air into the mixed ethanol solution. For constant-current configuration, a commercial source meter (Keithley 2400 Source Meter) was employed to measure and collect the electrical signals of f-CNTs sensors. The experimental setup was illustrated in Fig.2.

After the fabrication of alcohol vapor sensors, we conducted several experiments to characterize the f-CNTs based devices. Corresponding results are presented below.

B. *I-V Characteristics*

The I-V characteristic of a typical f-CNTs based sensor is shown in Fig. 3. Compared to the Ohm's law expectation (i.e., the red line), experimental results shows that f-CNTs exhibit linear I-V relationship at first, and self-heating effect starts at around several tens of μA. Then, in the nonlinear region, the resistance drops as temperature rises. In our application, operating currents are well-controlled under 10 μA, i.e., within the linear region of f-CNTs.

The power consumption of the f-CNTs based alcohol sensors are typically around several μW. This ultra-low power

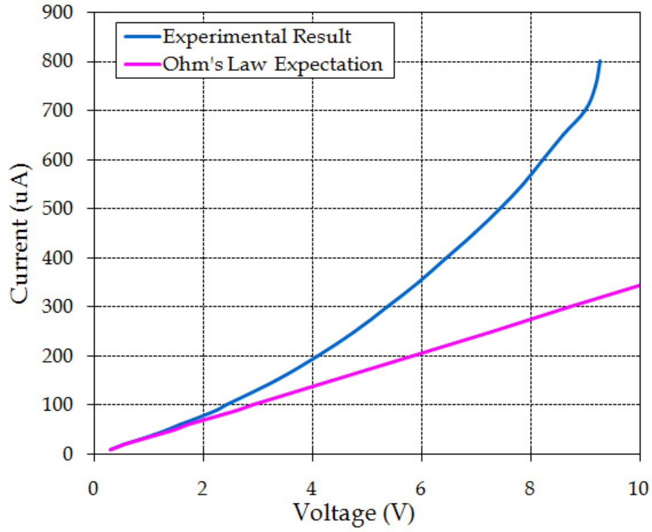

Figure 3. I-V characteristic of f-CNTs with COOH group.

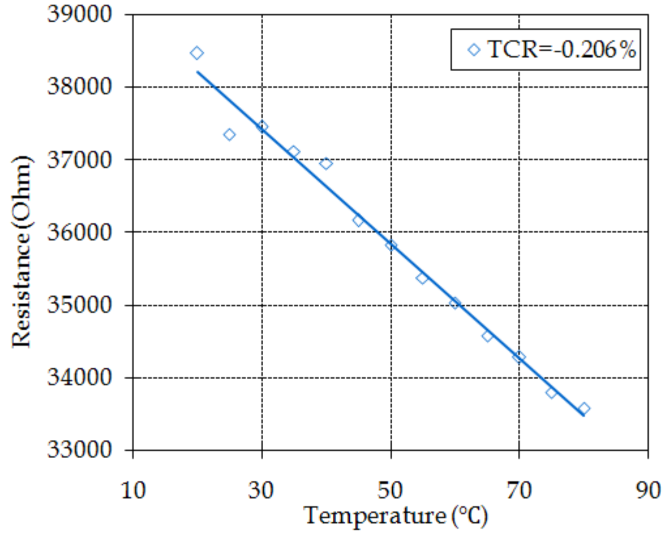

Figure 4. TCR of f-CNTs with COOH group.

consumption enables the sensor to pick up the physical parameters with minimal thermal disturbance [15], which is an indispensable property for sensing true measurands in micro scale world.

C. *Thermal Sensitivity*

Temperature coefficient of resistance (TCR) was tested to determine the temperature-dependency of f-CNTs. The Thermal sensitivity was calculated by (1):

$$R = R_{ref}[1 + \alpha(T - T_{ref})] \quad (1)$$

where α represents the temperature coefficient of f-CNTs based devices, R and R_{ref} represent the resistance at a certain temperature T and reference temperature T_{ref}, respectively.

During the TCR test, the f-CNTs based device was exposed to a temperature range of 20°C to 80°C at 5°C increments. During this period, humidity was controlled to be

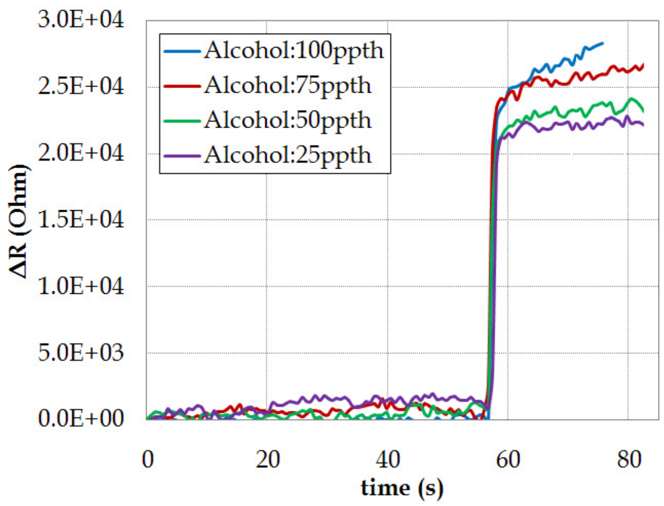

Figure 5. Typical response of f-CNTs based alcohol vapor sensor.

constant at 20%RH. The resistance change was recorded in Fig. 4 and a negative TCR of -0.206% was observed, which is in accordance with the trend of resistance dropping under higher current in the I-V characterization.

D. Typical Response

The proposed mechanism of f-CNTs based alcohol vapor sensor is that COOH group attached on the CNTs would interact with OH group of ethanol molecules in the ambient environment through hydrogen bonds, which leads to the change of alignment of the whole f-CNTs network, and further results in the resistance change of the alcohol vapor sensor. The main chemical reaction is given below:

$$\text{-COOH+OH}^- \longrightarrow \text{-COO}^- \text{+H}_2\text{O}$$

Upon exposure to the alcohol vapor, a sharp increase of the sensor resistance was observed. Fig. 5 illustrates the response of a typical alcohol sensor towards different alcohol concentrations. All four curves demonstrated a short response time. We also found that the change of resistance is reversible. After each measurement, the ethanol solution was withdrawn and compressed air was blown onto the alcohol sensor surface for several seconds, during which resistance dropped instantly. Despite of the resistance drift, the decreasing resistance usually stopped at almost the same level as its original value. However, in order to make sure that the sensor has been reset to its initial condition, a high current, i.e., 100 µA to 200µA, was added to anneal the sensor for the purpose of burning out all the ethanol molecules attached to the f-CNTs.

III. CONSTANT POWER CIRCUIT FOR ALCOHOL VAPOR DETECTION

As we presented earlier, during the alcohol vapor detection under constant-current configuration, the sensor respond to the alcohol vapor by a rising of resistance. However, this response would also result in the increase of power dissipation, most of which are in the form of heat. It is known that self heating of a sensor will introduce many problems such as larger noise level. The situation is even worse for f-CNTs based alcohol sensors, since the heat generated would possibly burn out the ethanol molecules that already attached to the sensor surface, which in turn leads to inaccurate measurements. Hence, in order to address the problem and keep the power dissipated on CNTs sensor constant, a circuit for constant-power operation was built and utilized to achieve better sensor performance.

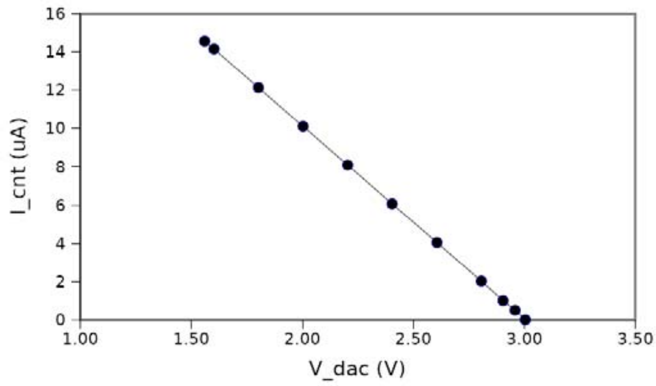

Figure 6. Relationship between I_{cnt} and V_{dac} in constant-power circuit.

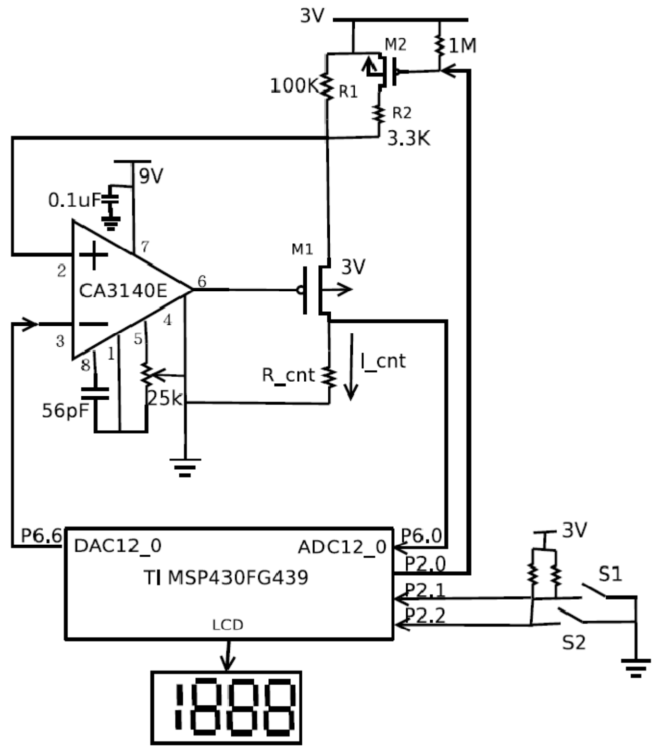

Figure 7. Circuit diagram: Voltage controlled current source and MSP430 micro-controller. .

In this design, a voltage controlled current source (VCCS) was implemented. The system was controlled by the MSP430 uP form TI. During measurement period, the gate voltage of M2 remains high and thus no current in this path. When the voltage output at DAC12 increases, the output voltage of the op-amp (V_) also increased. The system will eventually reach a stable point when current through M2 stops increasing. The relationship between I_{cnt} and V_{dac} is shown in Fig. 6 and represented in (2):

$$I_{cnt}=K\times V_{dac}+C \quad (2)$$

The TI MSP430FG430 is a 16-bit high end micro controller for Digital Multi-Meter (DMM) of DAC and 16channels ADC all in 12 bits resolution, for analog design. An evaluation board from SoftBaugh (DG 439V) powered by a 3V battery was also interfaced to the VCCS circuit in this design. To reduce power consumption, the uP will measure the CNTs sensor resistance and adjust the DAC output four times per second. For rest of the time, the uP will be in Low Power Mode 3 (LPM3) which consumes less than 3μW according to the TI document. The program flow of the MSP430 application is shown in Fig. 7.

This circuit setup has been used to measure the resistance of CNTs sensors under room temperature. During the measurement, data are digitally displayed on a LCD, and resistance change curve are shown on the computer simultaneously by the compatible software. In addition, the constant-power circuit enables the sensor to perform under different power levels, ranging from 0.05μw to around 2μw, which is convenient to investigate the relationship between the sensor performance and operating power. It is also noted that although self-heating can possibly affect the accuracy of measurement, it can be utilized, on the other hand, to clean up the residual ethanol molecules attached on the carbon nanotubes. Therefore, the constant-power circuit also offers the function to anneal the sensor after each cycle of measurement.

To sum up, the main functions of the constant-power circuit includes constant-power operation, data collection, operating power control and sensor annealing.

IV. Comparison Between Constant-Current and Constant Power Configuration

The sensing capability and the selectivity of the f-CNTs based alcohol vapor sensor have been proved in our previous work [12]. In order to evaluate the performance of alcohol vapor sensor with constant-power circuit, comparison experiments with constant-current configuration were conducted. In the experiment setup of constant-power configuration, constant power circuit was employed to replace the source meter in the constant-current mode. Other than that, all the variables remained the same for consistency.

A. Sensor Response Versus Power

In the experiments of constant-power mode, alcohol vapor sensors were operated under different power levels. Besides, we also applied different alcohol concentrations to the sensor. In Fig. 8, sensor responses versus different power units under four alcohol concentrations were investigated. The alcohol vapor concentrations used were 100ppth, 75ppth, 50ppth, and 25ppth, respectively. The sensor response was defined by (3):

$$Response=\frac{\Delta R}{R}\times 100\% \quad (3)$$

where ΔR stands for resistance change and R_0 represents the initial resistance.

In Fig. 8, the blue and orange lines represent the constant-

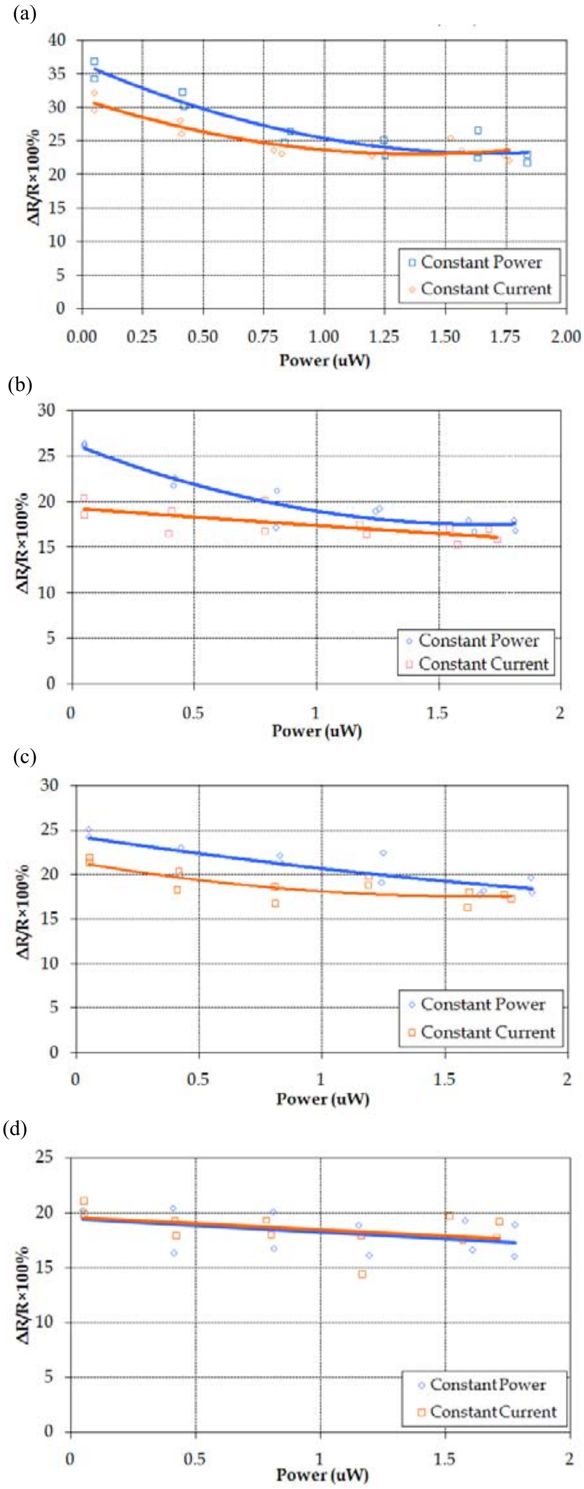

Figure 8. Response of alcohol vapor sensor under different operating power. Alcohol vapor concentrations: (a) 10%, (b) 7.5%, (c) 5%, (d) 2.5%.

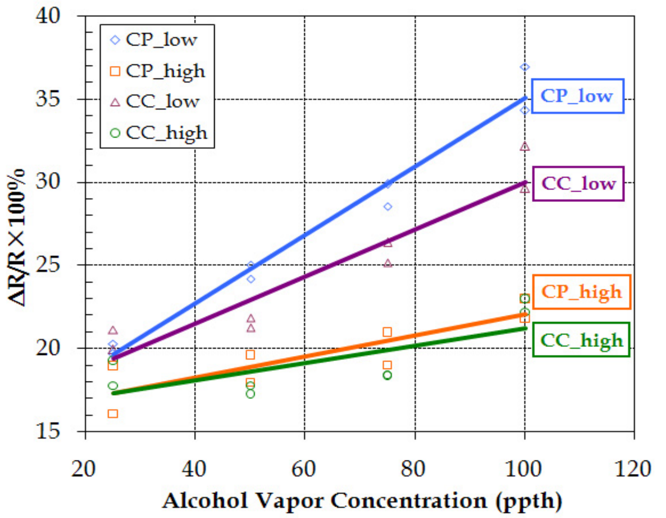

Figure 9. Responses of f-CNTs sensors under different alcohol vapor concentrations.

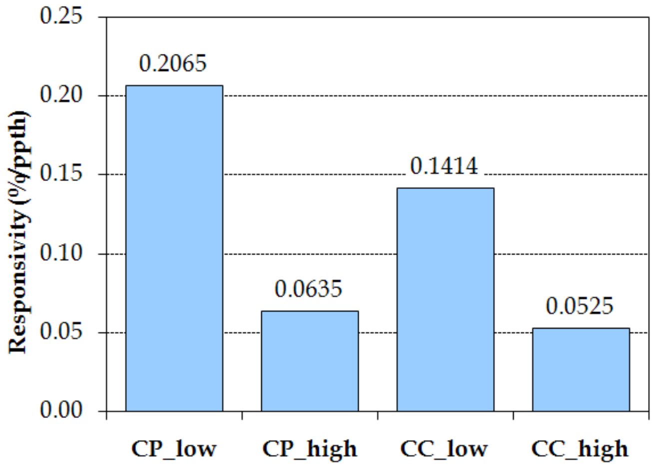

Figure 10. Responsivity of alcohol vapor sensors under different conditions.

power and constant-current configurations, respectively. The trends of both curves in Fig. 8 (a) to (d) proved a decrease of response along with the increase of operating power, which implies that the f-CNTs based alcohol sensor tends to perform better under lower operating power. In addition, it is also clearly illustrated in the figure that the alcohol sensor exhibits larger response under constant-power configuration rather than constant-current mode. However, when the concentration of alcohol vapor is relatively small, e.g., 25ppth, two response curves almost overlapped, i.e., both configurations exhibit similar response. To sum up, compared to constant-current configuration, the advantage of constant-power mode is more obvious under two conditions: lower operating power and higher alcohol vapor concentration.

B. *Responsivity*

Fig. 9 shows the comparison of four groups of measurement specifying different conditions: *CP_low*, *CC_low*, *CP_high*, and *CC_high*, where *CP* and *CC* stand for

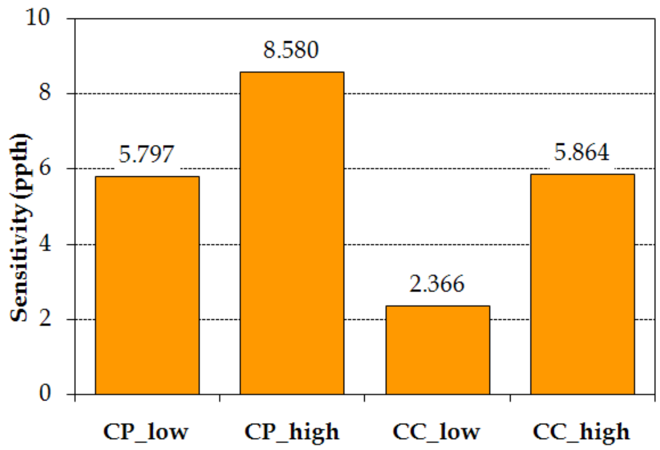

Figure 11. Sensitivity of alcohol vapor sensors under different conditions.

the constant-power and constant-current configurations, respectively, while *low* and *high* refer to the operating power of ~0.05uW and ~1.8uW respectively. For each specified condition, sensor responses under different alcohol vapor concentrations were illustrated in the figure. The slope of the figure implies the sensor responsivity, which is defined by (4):

$$Responsivity = \frac{Response\ of\ the\ sensor}{Alcohol\ vapor\ concentration} \quad (4)$$

Fig. 9 compared the responsivities of these four groups, with quantified values illustrated. The comparison results are presented below:

CP_low>CC_low>CP_high> CC_high

The largest responsivity is found in *CP_low* with the value of 0.2065%/ppth, followed by *CC_low* as 0.1414%/ppth. On the other hand, *CP_high* and *CC_high* exhibit similar responsivities and both much smaller than *CP_low*. We noted that *CP_low* demonstrated largest responsivity as well as the fact that both *CP_low* and *CC_low* proved better responsivity are in accordance with the conclusion we drew in the previous section.

C. *Sensitivity*

All sensors produce some output noise in addition to the output signal [16]. The factor of responsivity alone, however, is not enough to judge the sensor performance. Despite of the large resistance change rate, noises during measurements could disturb the true signal severely and jeopardize the accuracy of the sensor. In this case, the sensitivity of the alcohol sensor was evaluated (See Fig. 11). In this paper, we calculated the sensitivity by the following formula (5):

$$Sensitivity = \frac{Noise}{Responsivity} \quad (5)$$

By this definition, the sensitivity of the sensor reflects the smallest detectable alcohol vapor level, i.e., the smaller the calculated value, the higher the sensitivity. Fig. 10 shows the sensitivity of CNTs sensor under four conditions, the results are listed below:

$$CC\_low > CP\_low > CC\_high > CP\_high$$

Among the four specified conditions, *CC_low* exhibits the highest sensitivity as 2.366ppth, followed by the similar sensitivity of *CP_low* and *CC_high*, of which the sensitivities are almost the same. Compared with the responsivities in Fig. 10, we found that although *CP_low* proved best responsivity, its sensitivity, however, is not as good as *CC_low*. The possible reason is that constant-power circuit introduces larger noise level than constant-current mode, especially under lower operation power. It is reasonable because the constant-current configuration, i.e., the commercial source meter utilized, provides better noise reduction system than the constant-power circuit we built. Therefore, better sensitivity was found in *CC_low* instead of *CP_low*. However, the sensitivity could be potentially improved if we have better control of the noise level, i.e., better noise reducing component in the constant-power circuit.

V. Conclusion

Chemical sensors, batch fabricated by forming bundles of chemically functionalized multi-walled carbon nanotubes along the Au electrodes on SiO2/Si substrates using dielectrophoresis technique, were developed for alcohol vapor detection. The characteristics of f-CNTs with COOH groups are explored. Negative TCR were found. We observed the reproducibly resistance increasing of these f-CNTs sensors upon exposure to different alcohol vapor concentrations. The responses of the sensor were studied both in a constant-current configuration with the use of a Keithley 2400 Source Meter as well as a constant-power circuit. However, although operating with constant-power configuration under low power exhibits the largest responsivity, the sensor performance is limited by noise induced. Hence, better noise reducing component in the constant-power circuit would possibly enhance the resolution of our alcohol vapor sensor.

References

[1] Ray H. Baughman, Anvar A. Zakhidov, and Walt A. de Heer, "Carbon Nanotubes—the route toward applications", *Science*, Vol. 297, pp. 787-792, 2002.

[2] S. Reich, C. Thomsen, and J. Maultzsch, *Carbon nanotubes, basic concepts and physical properties.* Berlin: WILEY-VCH, 2004, pp. 3-30, 60-65.

[3] J. Kong, N.R. Franklin, C. Zhou, M.G. Chapline, S. Peng, K. Cho, and H. Dai, "Nanotube Molecular Wires as chemical sensors," *Science*, Vol. 287, pp. 622-625, 2000.

[4] Seongjeen Kim, "CNT sensors for detecting gases with low adsorption energy by ionization", *Sensors*, Vol. 6, pp. 503-513, 2006.

[5] Meng-Hung Tsai, Hong-Ming Lin, Wen-Li Tsai, and Yeukuang Hwu, "Examined the gas absorption properties of single wall carbon nanotube bundles by X-ray absorption techniques", *Rev. Adv. Mater. Sci*., Vol. 5, pp. 302-305, 2003.

[6] Wei Shi, and J. Karl Johnson, "Gas adsorption on heterogeneous single-walled carbon nanotube bundles", *Phy. Rev. Lett*., Vol 91, pp. 015504 1-4, 2003.

[7] A. Fujiwara, K. Ishii, H. Suematsu, H. Kataura, Y. Maniwa, and S. Suzuki, etc., "Gas adsorption in the inside and outside of single-walled carbon nanotubes", *Chem. Phy. Lett*. Vol. 336, pp. 205-211, 2001.

[8] O.K. Varghese, P.D. Kichambre, D. Gong, K.G. Ong, E.C. Dickey, and C.A. Grimes, "Gas sensing characteristics of multi-wall carbon nanotubes", *Sensors and Actuators B*, Vol. 81, pp. 32-41, 2001.

[9] Keat Ghee Ong, Kefeng Zeng, and Craig A. Grimes, "A Wireless, passive carbon nanotube-based gas sensor", *IEEE Sensors Journal*, Vol. 2 , pp. 82-88, 2002.

[10] Kay Hyeok An, Seung Yol Jeong, Ha Ryong Hwang, and Young Hee Lee, "Enhanced sensitivity of a gas sensor incorporating single-walled carbon nanotube-polypyrrole nanocomposites", *Adv. Mater*. Vol. 16, pp. 1005-1009, 2004.

[11] Junya Suehiro, Guangbin Zhou and Masanori Hara, "Fabrication of a carbon nanotube-based gas sensor using dielectrophoresis and its application for ammonia detection by impedance spectroscopy", *J. Phys. D: Appl. Phys*, Vol. 36, pp. L109-L114, 2003.

[12] Mandy L.Y. Sin, Gary C.T. Chow, Gary M.K. Wong, Wen J. Li, Philip H.W. Leong, and K.W. Wong, "Ultra-low-power alcohol vapor sensors using chemically functionalized multi-walled carbon nanotubes", *IEEE Trans. on Nanotechnology*, accepted, 2007.

[13] Mandy L.Y. Sin, Gary C.T. Chow, Carmen K.M. Fung, Wen J. Li, Philip H.W. Leong, K.W. Wong, and Terry Lee, "Ultra-low-power alcohol vapor sensors based on multi-walled carbon nanotube", *IEEE Int. Conf. on Nano/Micro Engineered and Molecular Systems,* pp.1198-1202, Jan. 18-21, 2006.

[14] Mandy L.Y. Sin, Gary C.T. Chow, M.K. Wong, Wen J. Li, Philip H.W. Leong, K.W. Wong, and Terry Lee, "Chemically functionalized multi-walled carbon nanotube sensors for ultra-low-power alcohol vapor detection", *IEEE Int. Conf. on Nanotechnology,* Vol. 2, pp.461-464, 2006.

[15] Victor T. S. Wong and Wen J. Li, "Bundled carbon nanotubes as electronic circuit and sensing elements", *IEEE- ICRA*, Vol. 3, pp. 3648-3653, 2003.

[16] Jon S. Wilson, *Sensor technology handbook*, Amsterdam, Boston Elsevier, 2005, pp. 3.