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Ultra-Low-Power Alcohol Vapor Sensors Based on Multi-Walled Carbon Nanotube

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Abstract*—We have demonstrated multi-walled carbon nanotube (MWCNTs) based sensors, which are capable of detecting alcohol vapor with ultra-low power. We fabricated the Si-substrate sensors using an AC electrophoretic technique so as to form bundled MWCNTs sensing elements between Au microelectrodes. The I-V measurement illustrates that we can activate the sensors at the Ohmic region of the sensors (at 10μA), which is without any overheat effect. The sensors only need an ultra-low power (~1μW) to detect the alcohol vapor. They exhibit fast, reversible and repeatable response. We have tested the response of the sensors with alcohol concentrations from 10ppth to 400ppth (ppth = parts per thousand). Our result shows that there is a linear relation between the resistance of the sensors and alcohol concentration. Also, we can easily reverse the sensor to the initial reference resistance by annealing them at 100-250μA current within 6 minutes. Moreover, the sensors are selective with respect to flow from air, water vapor, and alcohol vapor. Finally, we have also studied how the temperature of the sensors affects their response towards alcohol vapor. The result shows that the performance of the sensors will deteriorate as the temperature of the sensors increase. Also, the cooling effect of the vapor is not a dominating factor in determining the response of the sensor. Based on our experiments, we prove the feasibility of turning the MWCNTs sensors into a commercialized alcohol sensor with ultra-low power requirements.

Keywords-carbon nanotubes; alcohol sensor; ultra-low-power

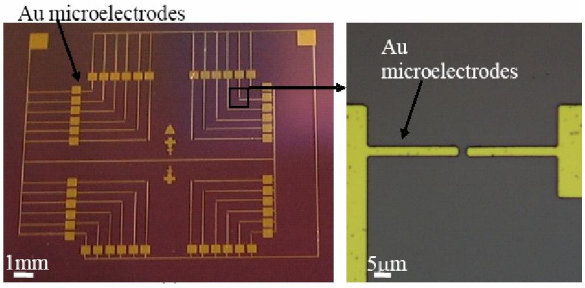
I. INTRODUCTION

MEMS (micro electro-mechanical systems) technology can provide low power consumption, low cost, high sensitivity, and portable sensors for in-situ chemical analysis in many areas like environmental control and monitoring, and personal safety [1-3]. One-dimensional effects in carbon nanotubes (CNTs) make them potential materials for the development of MEMS sensors. Not only do they have promising structural, mechanical, and electrical properties, but they also have nano-sized morphology and a high surface-to-volume ratio, which results in highly sensitive and rapid gas adsorption [4]. A naval research laboratory in the USA [5] has shown that the capacitance of single-walled carbon nanotubes (SWCNTs) thinly coated with chemoselective materials is sensitive to a wide range of chemical vapors. Also, Someya and co-workers have exhibited the feasibility of using SWCNTs in a field-effect transistor (FET) configuration as alcohol sensors [6].

Our recent experimental findings show that the MWCNTs based sensors can detect alcohol vapor with high repeatability and ultra-low power consumption. In this paper, we will report the development of the MWCNTs based alcohol sensors. We will first describe the experimental setup. Then, we will show the I-V characteristic of the sensors and the selectivity of the sensors towards alcohol vapor over flows of compressed air and water vapor. We will also illustrate the relationship between the sensors' resistance changes to the alcohol vapor concentration and how the sensors' reference resistance can be recovered after each measurement. Finally we will present how the temperature of the sensors can affect their performance which will then give us a clearer picture on how the alcohol vapor is adsorbed onto the MWCNTs.

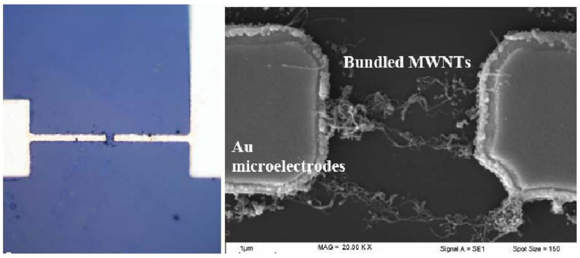
II. SENSOR FABRICATION

The Au microelectrodes were first fabricated on the Si-substrate by a lift-off process as shown in Fig. 1. The MWCNTs (from the Sun Nanotech Company Ltd., Beijing, China) were then batch manipulated along the microelectrodes by AC electrophoresis according to our previous paper [7]. Fig. 2 shows the optical and scanning tunneling electron microscopic images of our sensor.



(a) (b)

Figure 1. (a) Photograph of the fabricated array of Au microelectrodes on a Si substrate. (b) Optical image showing a pair of Au microelectrodes before CNTs manipulation.



(a) (b)

Figure 2. (a) Optical microscopic image and (b) Scanning electron microscopic (SEM) image showing the formation of MWCNTs between a pair of parallel Au microelectrodes.

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III. EXPERIMENTAL SETUP

The experimental setup is shown in Fig. 3. The organic chemical we used for the ethanol solution was absolute ethanol (from Merck Ltd., 99.9%). We prepared the ethanol solution by mixing different volume ratios of ethanol and DI-water (> 15MOhm-cm). The alcohol vapor was generated by directing a well-controlled flow of compressed air into the mixed ethanol solution. The sensors were tested with alcohol vapor concentration from 10ppth to 400ppth. We calculate the alcohol concentration by the following equations:

$$1ppth = 1\ part\ in\ 10^3 = 1\,millilitre(mL)\ per\,litre \quad (1)$$

As the total volume of solution used in our case is 200mL, equation (1) can be rewritten as:

$$1ppth = 0.2mL\ ethanol\ solution\ per\ 200mL \quad (2)$$

So, an ethanol solution of 10ppth can be made by mixing 2mL of absolute ethanol with 198mL of DI-water.

The Si-substrate chip was wire-bonded to a PCB board. An airtight plastic cover was put on top of the sensor chip. Ten holes (diameter of 1.2mm) were drilled on the PCB board, which were around our sensor chip, for the outlet of the vapor. With the use of a Keithley 2400 SourceMeter, we studied the response of the sensors in a constant current configuration. We took the data every 0.7 second. We define two currents here so as to make the explanation below clear. The first one is $I_{measure}$, which is for the activation of the sensors. The second one is I_{anneal}, which is for the annealing of the sensors so that they can be returned to their initial resistance. All experiments were performed at room temperature of 23-25°C.

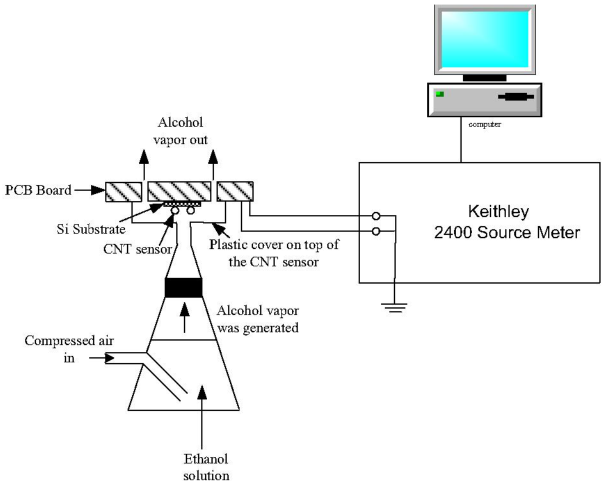

Figure 3. Schematic diagram showing the experimental setup for detecting alcohol vapor.

IV. EXPERIMENTAL RESULTS

A. Power Consumption

Electrical properties of individual CNTs have been studied by many research groups [8-9]. Their reports always show their microwatt power characteristics. Although bundles of MWCNTs are complex networks of individual CNTs, they also show a similar behavior as stated in our previous paper [10]. But, from our experience, the performance of these bundles can have large variations. So here, we will first examine the I-V characteristics of our bundled MWCNTs sensors using a constant current configuration. The I-V measurement is shown in Fig. 4. Similar to other previous reports, self-heating effects started at 80μA and 1.5V. This reveals that we can treat the bundled MWCNTs as a resistive element with an ultra-low power requirement. In most of the experiment reported here, we activate the sensors at the linear region of 10μA with a power consumption of only ~1-2μW.

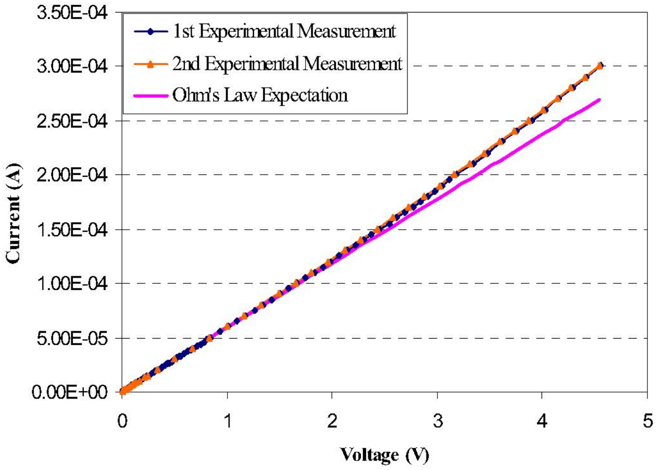

Figure 4. I-V characteristics of the MWCNTs bundles. Two repeated measurements were performed to validate the repeatability. The straight line is the theoretical expectation using Ohm's law.

B. Typical Response

Fig. 5 shows the observed response of the sensor at 25°C when alcohol vapor at 400ppth was blown onto the sensor. A typical MWCNTs sensor itself has fluctuations of only about 0.25% of the average value of R_0 (from t = 0 to 60sec). A sharp response was observed within 1s after we delivered alcohol vapor into the chamber. We filled the chamber with the alcohol vapor for 10s. We related the response of the sensors towards this resistance change (ΔR).

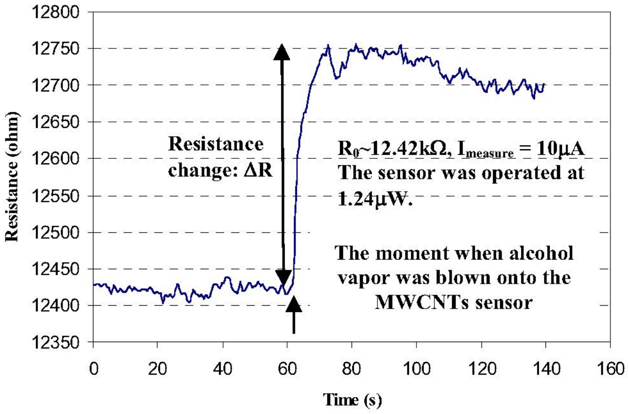

Figure 5. Observed resistance change of the MWCNTs sensor with the introduction of 400ppth concentration of alcohol vapor.

C. Selectivity

We also compared the response of the MWCNTs sensor to the flow of compressed air, water vapor, and alcohol vapor. When we blow the alcohol vapor onto the MWCNTs sensors, 3 factors will affect the observed response i.e. the increase in sensor resistance (ΔR). The first one is the air flow itself. From our previous findings [7], we know that MWCNTs are sensitive to the change of temperature and their resistance drops with increasing temperature. As the vapor flowing on the sensors will convectively take away an amount of heat from them, it will enhance the signals by a certain amount as well. The second one is the DI-water used to mix with the absolute ethanol. As most of the concentration of the alcohol vapor we tested is not very high, a very large volume ratio of the ethanol solution will be the DI-water. If the MWCNTs are more sensitive towards the DI-water than the absolute ethanol, it will severely affect our results. The third one is the absolute ethanol, which is what we want to measure. We compare the response of these three kinds of vapor by using the same experimental setup except that the ethanol solution was replaced with the compressed air and DI-water respectively. So, we can separately assess the contributions of these 3 kinds of vapor towards the observed response. As shown in Fig. 6, the signal of the alcohol vapor is easily distinguishable from those due to the flow of compressed air and water vapor as the response from the 200ppth alcohol vapor was about 100% larger than the other two kinds of vapor. So, this confirms that the MWCNTs are really detecting the ethanol molecules from the ethanol solution. This promising result encourages us to further investigate the response of the sensors towards other alcohol concentrations.

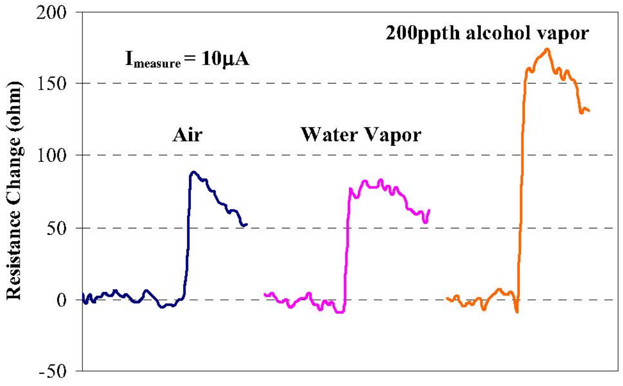

Figure 6. Comparison of the response of the MWCNTs sensor towards the flow of compressed air, water vapor, and alcohol vapor.

D. Alcohol Sensing Ability

A similar measurement to the one mentioned in Part B was carried out under the exposure of alcohol vapor from concentrations of 10ppth to 400ppth. Three cycles of data were done at each concentration. The dependence of the sensitivity of the sensor on the concentration level of alcohol vapor is shown in Fig. 7. It shows that the sensor responds linearly with the alcohol vapor concentration. The sensor has very good reproducibility as the fluctuations of the relative resistance change at all concentrations are within 10% of the corresponding average values. It also shows that the sensor is still sensitive with 10ppth alcohol vapor because the sensitivity at 10ppth (~0.3%) is larger than the fluctuations of the sensor itself (~0.25%). It should be noticed that at concentration below 100ppth, the sensing response will not be very accurate as it will be influenced more significantly by the signals from the air flow and the DI-water. So, in the future, we will try the chemically functionalized MWCNTs so as to enhance their sensitivity and accuracy.

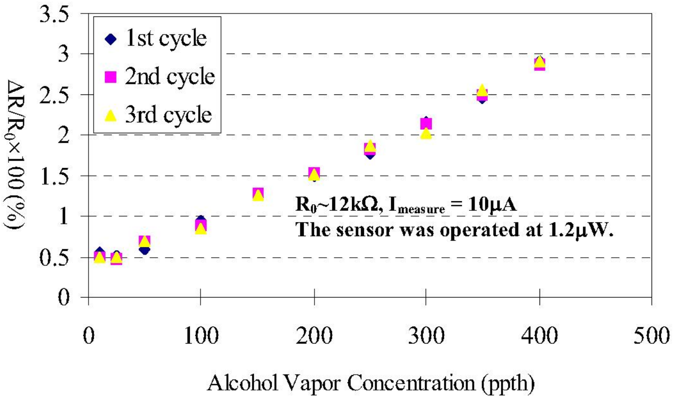

Figure 7. Measured relative resistance change, $\Delta R/R_0$, of the MWCNTs sensor to 10-s dose of alcohol vapor with concentrations from 10-400ppth. Three cycles of measurement have been done.

E. Reversibility

We found out initially that the sensors would not return to its initial resistance value for at least 2 hours even after the source of alcohol vapor was removed. Although we still do not fully understand the working principle, i.e., whether the alcohol vapor are physically or chemically adsorbed onto the MWCNTs, the increase in resistance we have observed in all measurement must be due to the ethanol molecules being adsorbed onto the MWCNTs. So, we speculate that the reversibility could easily be obtained by burning the sensor to a high enough temperature. Fig. 8 shows how we perform the experiment with an annealing current (I_{anneal}) of 100μA. We first took 100 data points at 100μA for reference at the beginning (Region A). Then we applied 10sec dose of alcohol vapor onto the sensor with $I_{measure}$=10μA. At last, we burned the sensor at 100μA and recorded the annealing time (t_{anneal}), which is the time for it to return back to the initial resistance (Region B). Fig. 9 shows the relationship between t_{anneal} and I_{anneal}. We have tested on 3 different alcohol vapor concentrations (50, 100, and, 150ppth) and burned the sensor with I_{anneal} = 100, 150, 200, and, 250μA respectively. As expected, the higher the I_{anneal} (higher over-heat temperature), the lower the t_{anneal} and the higher the alcohol concentration, the higher the t_{anneal}.

F. Temperature Effect on the Alcohol Sensing Ability

As mentioned in [7], we know that the resistance of the MWCNTs sensors drops as the environmental temperature increases, i.e., negative temperature coefficient of resistance (TCR). So, we want to study how the temperature (resistance) of the sensors affects its alcohol sensing ability. We did the experiment by applying 10-sec dose of 100ppth of alcohol vapor with different $I_{measure}$ (from 5-250μA). As shown in Fig. 10 for the "with power" case, once the current went up to the overheat region (at 80μA from Fig. 4), the resistance change due to the alcohol vapor dropped more significantly. The higher the current passing through the MWCNTs, the lower the resistance change. It is reasonable because hotter nanotubes will reduce the adsorption efficiency of the alcohol vapor.

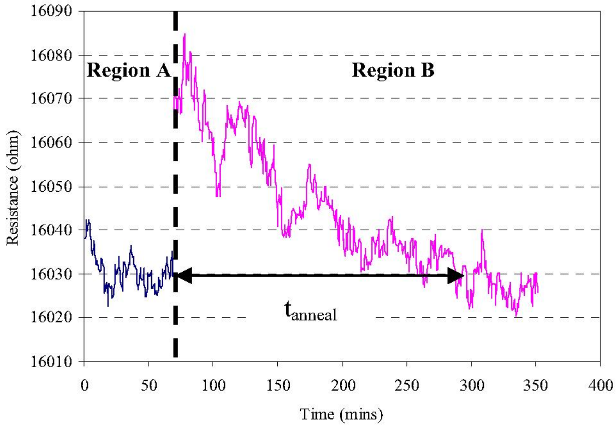

Figure 8. One example of the annealing process. It shows the observed response of the sensor when we burn the sensor with 100μA after the introduction of 10-sec dose of 50ppth alcohol vapor. We recorded the annealing time (t_{anneal}) from this graph.

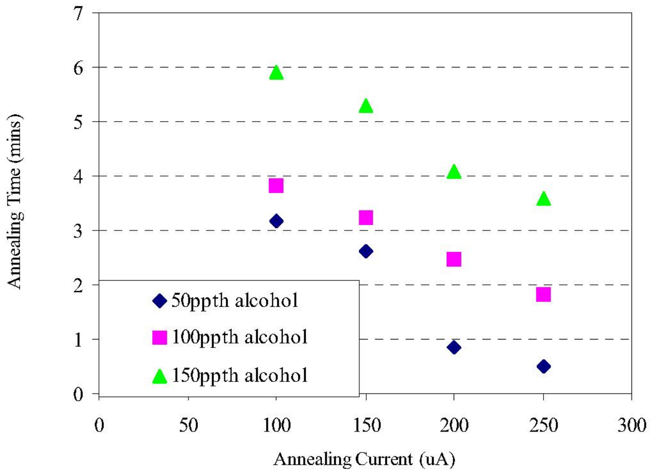

Figure 9. Relationship between the annealing time (the time for the sensor to return back to the initial reference resistance) and the annealing current (the current used to burn the sensor).

G. *Adsorption Mechanism of the Alcohol vapor*

In order to have more understanding on how the alcohol vapor is being absorbed onto the MWCNTs, we also compare the "with power" and "no power" cases. In the "no power" case, we applied the alcohol vapor onto the sensor at room temperature. We did this by first taking 100 data points for reference at one current. Then we turned off the power of the sensor and waited for 15mins so the sensor returned back to the room temperature. Afterwards, we introduced a 10-sec dose of 100ppth alcohol onto the sensor. Then we turned on the sensor immediately with the same current as before and recorded the resistance change in the sensor. Fig. 10 shows the experimental results. As the temperature of the ethanol solution is always at room temperature, the temperature difference between the sensor and the alcohol vapor must be larger in the "with power" case. If the cooling effect of the alcohol vapor is dominated, the resistance change in the "with power" case must be larger than the one with the "no power" case. But from "Region 2" where there is an overheat effect, the results are reversed from what we expected. So, we can conclude that the adsorption rate but not the cooling effect is the dominating factor in determining the response of the sensors. Also, as there is no overheat effect in "Region 1", the temperature of the sensor in the "with power" case must close to the room temperature. So, we can notice that there is not much difference in the resistance changes in both "with power" and "no power" cases.

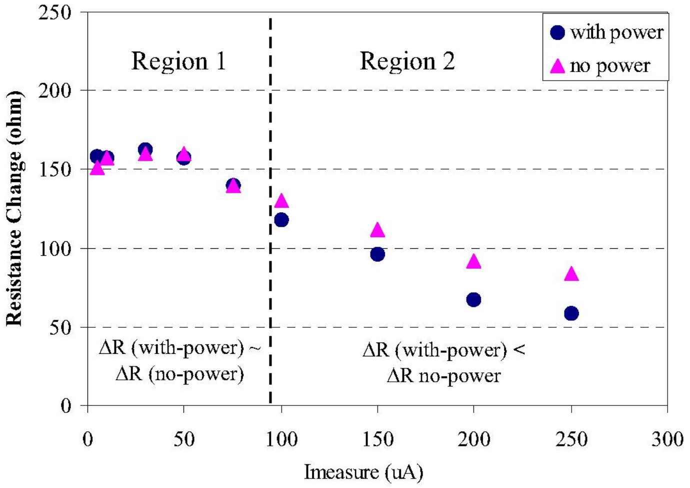

Figure 10. Response of the sensor with different $I_{measure}$. We have also compared its behavior on cases of "with power" and "no power". Overheat effect of the MWCNTs definitely has influence on the sensors' response towards the alcohol vapor.

V. CONCLUSION

We demonstrated the possibility of using MWCNTs based sensors as alcohol sensors. From the IV analysis, we know that the sensors can be operated at an ultra-low-power level (a few μW), which is very attractive for commercialization as it is 1000 times less than any commercial alcohol sensors. Our sensors also have a reproducible response towards different alcohol concentrations and they can be reversed back to the initial reference resistance very easily by annealing them at a high enough temperature. They also have selectivity towards different vapors. In the future, we will focus on how to increase the sensitivity of the sensors towards the alcohol vapor by chemically adding an appropriate functionalized group onto the MWCNTs.

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