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Reusable CNTs-Based Chemical Sensors

Mengxing Ouyang and Wen J. Li*

Centre for Micro and Nano Systems, The Chinese University of Hong Kong, Hong Kong SAR, P.R. China

***Abstract* — Recovery time, which is one of the key metrics in gauging sensor performance, is crucial for CNTs sensors since it directly affects the reusability, reliability and accuracy of the sensors during detection. Using the resistive f-CNTs based ethanol vapor sensor as an example, we proved that the annealing method of heating up the sensor with a sufficient high current for a certain time period can effectively facilitate the sensor return to its original status. During experiments, 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 ethanol vapor detection. In addition, experiments were carried out to determine the relationship between recovery time and other parameters during ethanol vapor detection, such as annealing current, exposure time, and ethanol vapor concentration.**

Keywords — ***Carbon nanotubes, functionalized CNTs Sensors, ethanol vapor detection, sensor recovery.***

I. INTRODUCTION

For the last decade, carbon nanotubes have been receiving considerable attention as the sensing element for MEMS sensors due to their extraordinary properties such as minute size of the sensing element and the correspondingly small amount of material required for a response [1]. However, CNT sensors suffer from several drawbacks, one of which is their slow recovery time after exposure to stimuli. Some researchers have reported that without any processing on the sensor, it takes about 12 hours for CNTs to return to the original base resistance [2]. In order to overcome this limitation, a variety of methods have been used, such as heating up the sensor for desorption of the chemical molecules [3, 4], ultraviolet (UV) light illumination [5], Pd modification of carbon nanotube [6], and exposing the sensor towards humid air instead of dry air [7]. However, most of those methods require extra components (e.g., UV source and microheater) or complex procedure (e.g., CNT modification and humidity control) to achieve the purpose of accelerating the recovery process, which not only complicates the fabrication process of the sensor, but also raises the cost of the sensor, and even might make the sensors implausible for applications that require ultra-small sensing systems. In our lab, without the requirement of further implementing any component, we use carbon nanotube itself as the heating element to anneal the sensor back to its original reference resistance and the recovery time is controlled by the annealing current we applied to the sensor.

In our previous research, we have investigated the sensing performance of f-CNTs based ethanol vapor sensors, which not only proved good responsivity upon exposure to ethanol vapors by exhibiting an immediate sharp resistance increase, but also demonstrated fast response time [8]. During experiments, we found that the natural recovery process of the f-CNTs sensor towards its initial status is time consuming and sometimes unreliable. In order to further enhance the sensor reusability as well as to improve sensing accuracy, we used an annealing method to treat the sensor after each measurement by applying a relatively high current to heat up the sensor for a few minutes to accelerate its recovery. In this paper, we will demonstrate that this method is effective during measurements. Besides, three parameters that relate to the recovery time will be discussed in detail.

II. SENSOR FABRICATION

A. Sensor Fabrication and Experimental Setup

In our research, DEP manipulation was used to form carbon nanotube linkage between microelectrodes, which were fabricated on Si substrate by photolithography procedure. Chemical oxidation method was used to graft COOH group along the sidewall and the tube ends of the MWNTs. During the DEP 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 will evaporate, and leave the f-CNTs connection between the two tips. This fabrication process has the advantages of simple fabrication procedure, low cost, and makes batch fabrication plausible.

After the successful fabrication of f-CNTs linkage, 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, for the purpose of electrically connection with the measuring unit. And then, a plastic cover was put on top of the sensor chip. During the experiments, the ethanol vapor as generated by directing a well-controlled flow of compressed air into the mixed ethanol solution. A commercial source meter (Keithley 2400 Source Meter) was employed to measure and collect the electrical signals of f-CNTs sensors under constant-current configuration. The experimental setup is illustrated in Fig. 1.

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**Contact author: Prof. Wen J. Li: wen@mae.cuhk.edu.hk.*

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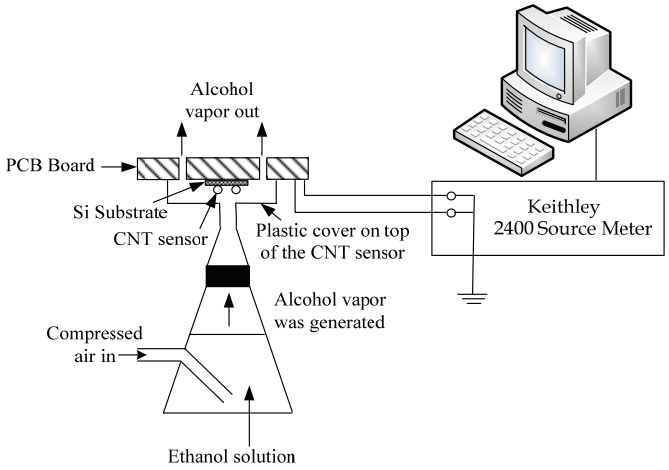


Fig. 1 Experimental setup of a constant-current f-CNTs ethanol vapor sensor.

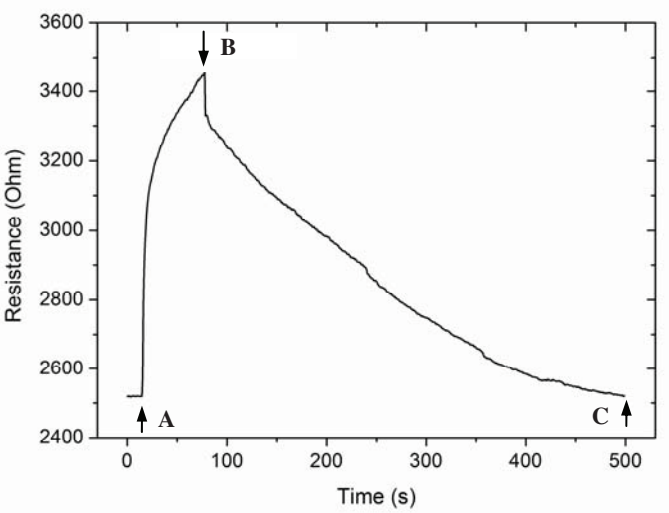


Fig. 3 Typical resistance change during ethanol vapor detection and recovery.

B. Sensing Mechanism

Fig. 2 shows a schematic diagram of how the ethanol molecules interact with the COOH groups through hydrogen bonds. We believe that with polar COOH groups attached onto the nanotube surface, the sensors will give stronger response towards the ethanol vapor as their absorption efficiency with these volatile organic molecules will be increased due to the fact that there are dipole-dipole interactions (mainly hydrogen bonding) between the COOH groups on the MWNTs and the polar organic molecules like ethanol. As illustrated in Fig. 2, the proposed mechanism of f-MWNTs sensor is described here: Once encountering the OH group of ethanol molecules in the ambient environment, the -COOH group attached to the carbon nanotubes would interact with the OH group through hydrogen bonds, which further leads to the resistance change of the ethanol vapor sensors. The main chemical reaction is given below:

$$-COOH+OH^{-}\rightarrow -COO^{-}+H_2O$$

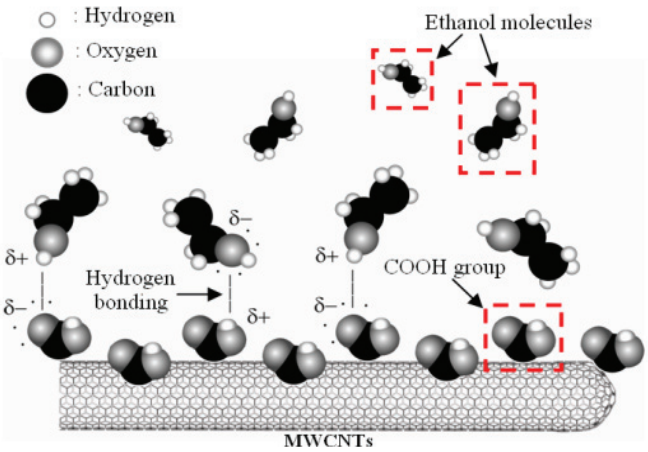


Fig. 2 Proposed Mechanism of f-MWNTs based Ethanol Vapor Sensing.

It has been noticed that the whole process is reversible if the ethanol molecules attached to the sensor surface are eliminated. During the experiments, we anneal the sensor by blowing the compressed air onto the sensor surface and apply relatively high current to heat up the sensor and clear up the residual molecules, where the previous method targets eliminates those molecules attached to the sensor surface physically while the latter approach untie the chemical bond between ethanol molecules and –COOH group.

III. Investigation of Sensor Recovery Process

During recovery of f-CNTs sensors, several factors would affect the recovery time: annealing current, exposure time and ethanol vapor concentration. In order to investigate how those parameters contribute to the recovery process, series of experiments were carried out.

For all the results presented in this section, we define the recovery time as the time interval that the sensor takes from the beginning of the annealing to the moment that it returns to the same resistance as the moment before it was exposed to ethanol vapor, i.e., the time interval between point B and point C as illustrated in Fig. 3. The reason that we use the above definition of recovery time is for the consistence of measurement and for the convenience during results comparison. However, we do realize that the comparison between resistance at point A and point C was conducted under different current (activating current at point A and annealing current at point C); it also has been noticed that at moment C, if we switch the current that applied to the sensor back to the activating current used at point A, the sensor resistance would increase for a certain value. This phenomenon could be expected from the negative Temperature Coefficient of Resistance (TCR) of the f-CNTs employed in our experiments. Moreover, based on this increased resistance only, we still lack evidence to prove whether the sensor has returned to its original status yet. Because after being heated-up during annealing process for several minutes, the temperature of the f-CNTs sensor is higher than ambient environment, i.e., room

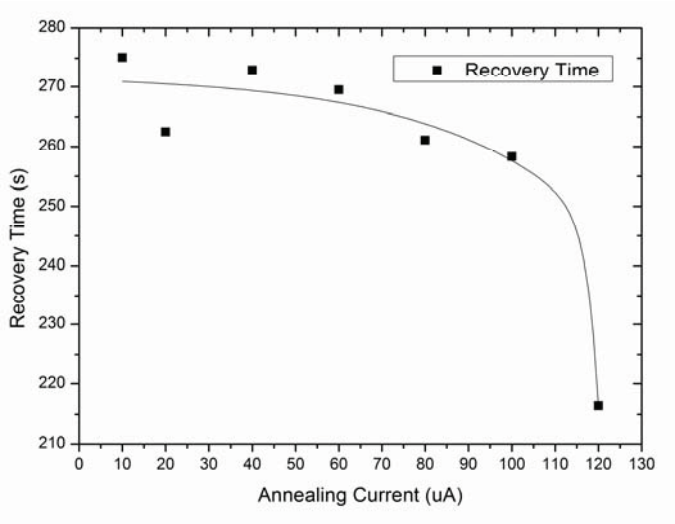


Fig. 4 Recovery time under different annealing current.

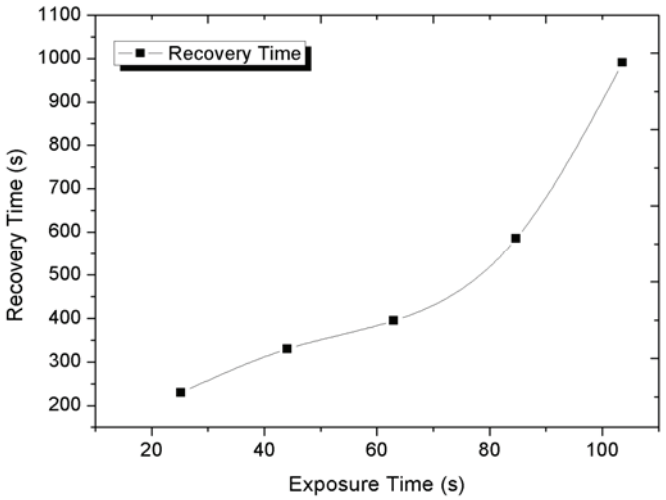


Fig. 5 Recovery time under different exposure time.

temperature in our case. Not to mention that under this circumstance, the instability of the sensor would jeopardize the sensor performance during the next cycle of measurement. However, according to our observation, after each recovery process, withdrawing the activating current and cool down the sensor for a while (~1-2 min) would stable the sensor and prepare it for a steady performance during further detection.

A. Typical Recovery Curve

As we mentioned previously, upon exposure to ethanol vapor, an instant sharp increase of resistance was observed. The process of ethanol vapor detection as well as the recovery of a typical f-CNTs sensor is illustrated in Fig. 3. At moment A, the sensor began exposure to ethanol vapor and exhibited a sharp resistance increase. After an exposure period of ~40 seconds, the ethanol vapor was withdrawn at moment B and the sensor was immediately activated with a relatively high current (e.g. 60μA in Fig. 3). Then, after ~420 seconds, the sensor gradually returned to its initial resistance. There are two main reasons that accelerate the decreasing of resistance once the sensor was heated up: The withdrawn of ethanol vapor that led the sensor to return to its original resistance, as well as the negative TCR of this kind of CNTs, i.e., the sensor resistance decreases in the non-linear I-V region due to heated temperature. Besides, higher energy stored on the sensor surface can also burn out the residue ethanol molecules attached onto the sensor surface which speed up the annealing process. In the response curve shown in Fig. 3, an immediate shift of the sensor resistance at moment B was observed, which is due to the fact that at the very moment, the activating current, which was within the linear region, was changed to the annealing current, which was in the non-linear region. Therefore, the negative TCR of the sensor determined that the sensor resistance exhibited a sudden drop.

B. Recovery under Different Annealing Current

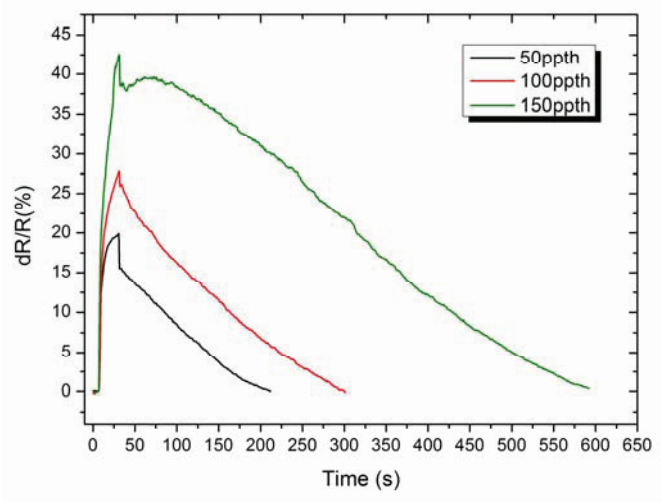
Fig. 4 illustrates the recovery time versus annealing current. During the experiment, the annealing current applied to the sensor ranged from 10μA to 120 μA, and as shown the corresponding recovery time under the annealing current of 120 μA could reduce the recovery time from ~275s to ~216s. The decreasing trend in the figure showed that the larger the current we applied to the sensor, the shorter the recovery time. Also, we presume that the dramatic decrease of recovery time between 100 μA and 120 μA was due to the over-heat effect of our f-CNTs sensors annealing within non-linear region, i.e., under the high annealing current. Previously, we have demonstrated in our work [8] that overheating the CNTs is not desirable for the operation of f-CNTs ethanol vapor sensors, as the sensors exhibited larger responsivity and shorter response time when operated in the linear I-V curve region. However, for recovery process, the overheating of the sensing element was utilized to further accelerate the sensor annealing.

We note here that, although larger annealing current results in a shorter recovery time, which is desirable for actual applications, an excessively high current also increase the risk of burning out part or the whole CNTs network, further leading to the fluctuation of sensor resistance and jeopardizing the detecting precision, or even cost the sensor. Therefore, it is essential to find the optimal annealing current during experiments in order not only to reset the sensor within shortest time period, but also to maintain the stability of the sensor.

C. Recovery under Different Exposure Time

Another factor that affect the recovery time of the f-CNTs sensor is the exposure time of the sensor towards ethanol vapor. To investigate the relationship between them, a f-CNTs sensor was exposed towards the same ethanol concentration (i.e., 100ppth) for different time intervals and the recovery time during each cycle of measurement were compared. In Fig. 5, while the exposure time was elongated from 25 s to 105s gradually with a step of 20 s, the recovery time increased from ~230s to ~991s. The activating current and the annealing

(a)



(b)

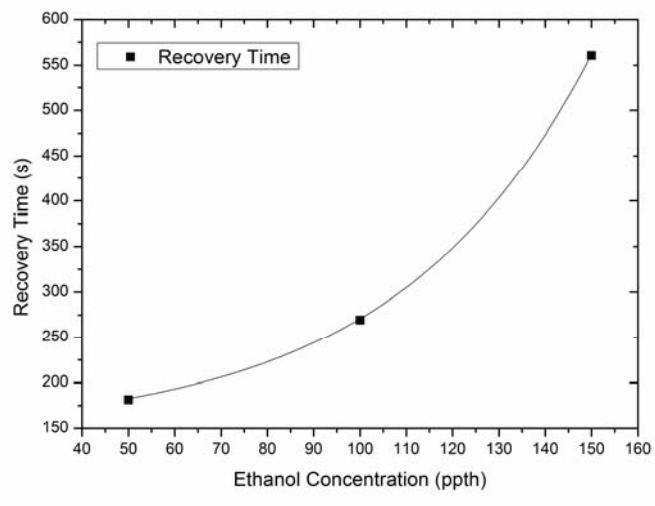


Fig. 6 (a) Response and recovery curve under different ethanol vapor concentrations; (b) Recovery Time versus ethanol vapor concentrations.

current used during the experiments were 1 μA and 30 μA, respectively. This result proves that longer exposure time towards chemical requires longer recovery time.

D. Recovery under Different Ethanol Vapor Concentration

In addition, experiments were carried out to determine the relationship between recovery time and ethanol vapor concentration. Other parameters such as exposure time and annealing current were kept constant during measurement. The sensor was exposed to ethanol vapor for ~20s under an activating current of 1 μA and then applied with an annealing current of 60 μA. The response curve using three ethanol vapor concentration (50ppth, 100ppth and 150ppth) were plotted in Fig. 6 (a) and the recovery time of each curve was calculated and compared in Fig. 6 (b). In the response curve under 150ppth, the resistance did not immediately decrease once the recovery process started as the other two curves. Instead, the resistance kept increasing for ~20s before it eventually began to drop. The explanation is that the high concentration

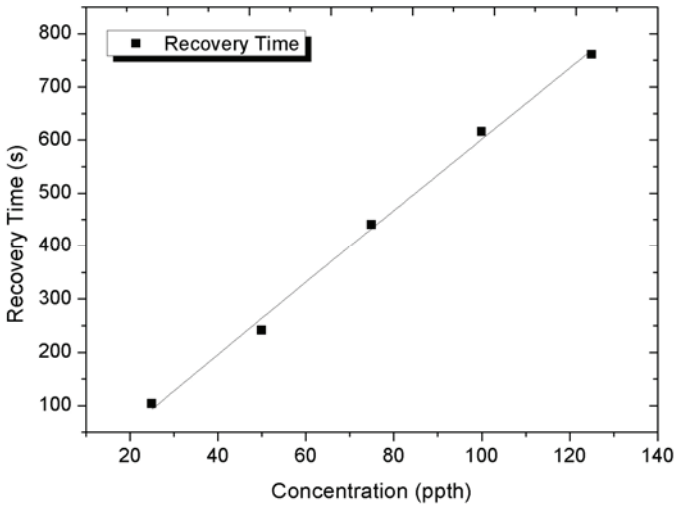


Fig. 7 Recovery time under different ethanol vapor concentrations.

(150ppth) still managed to have a strong influence on the sensor resistance for several seconds at the beginning of the annealing process, even if the sensor was already operated under a high current and was over-heated. Fig. 7 shows the detailed results of recovery time versus ethanol vapor concentration for another f-CNTs sensor. While the sensor was exposed to five different ethanol concentrations from 25ppth to 125ppth with a step of 25ppth, the recovery time using an annealing current of 30 μA increased from 104s to 761s. Results from both sensors reveal that longer recovery time is needed when sensor is exposed to higher ethanol vapor concentration.

IV. CONCLUSION

In order to overcome the limitation of long recovery time of the f-CNTs sensors, a successful attempt by means of using f-CNT itself as heating element to heat up the sensor after detection was investigated. Experimental results have proved that provided with sufficient annealing current, this method could effectively shorten the recovery time to the order of minutes (e.g. 5 min for our application) without fabricating or implementing additional heating component to the sensing system. Experiments proved that the larger annealing current, the shorter the recovery time. Moreover, longer exposure time and higher chemical concentration both require longer recovery time. For realistic applications, we should take into consideration all these factors and choose a well controlled and optimized annealing current that enable the sensor to recover within shortest time without causing instability or the burnt out of the CNTs sensing elements. In addition, the recovery process would be even more efficient if other annealing method were also employed, such as using dry air to blow on the sensor surface and cool down the sensor after each cycle of measurement, to guarantee the reset and the stability of the sensor status.

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