

Carbon Nanotubes Gas Sensor for Ethanol Detection

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Abstract-- Carbon nanotubes (CNTs), synthesized by thermal chemical vapor deposition, have been used to fabricate a prototype sensor. The sensor was investigated for its sensitivity towards different chamber pressure of ethanol vapor at room temperature. Upon exposure to a with and without ethanol environment at room temperature, the electrical resistance of the sensor was found to increase even for ethanol vapor chamber pressure as low as 50mTorr and to return back respectively. It is proposed that hydrogen bonding of the functionalized groups on CNTs with adsorbed molecules is responsible for this response.

Index Terms-- Carbon nanotubes, thermal chemical vapor deposition, gas sensor, hydrogen bonding

I. INTRODUCTION

Gas sensors used in many factories and hospitals are important to environmental monitoring. In order to prevent the gas from leaking and endangering the human body, it is necessary to detect chemical molecules and examine different gases. The extensive use of ethanol in research and industries demands for a sensitive sensor for its leakage detection. Although traditional gas sensors made by using semiconducting oxides or silicon based systems are inexpensive, safe and sensitive, they have been operated at high temperature to enhance chemical reactivity between the material and the target gas molecule. This major fault makes traditional gas sensors have a limit for future applications. The search for new materials operated at room temperature never ends. Carbon nanotubes (CNTs), in this stand, it has been concluded that the smaller material size, high chemical reactivity, good conductivity and high specific surface area would improve the sensitivity and response times of as-made gas sensors [1]. According to the electron-transmission mechanism on the surface of CNTs, the detected gas can be classified into reducing and oxidizing gaseous species. Being exposed to reducing gaseous species [2, 3], the electrical resistance of CNTs was found to increase, whereas which being exposed to oxidizing ones decreased [4, 5]. Gas sensing properties of the CNTs have been extensively studied [6-8]. Some groups have studied ethanol vapor sensing using polymer functionalized CNTs [7, 9] or metal nanoparticle/nanoclusters decorated CNTs at high temperatures [10]. In the present work, the electrical response

of carbon nanotubes (CNTs) thin film towards different chamber pressure of ethanol for gas sensing applications is reported.

II. EXPERIMENTS

A. Synthesis of functionalized carbon nanotubes

In this work, CNTs were synthesized by a thermal chemical vapor deposition (CVD) system. CVD process using Fe, Co, Ni, and alloys as the catalysts can be controlled by varying the size of metal catalyst. The silicon substrate was cleaned with standard Radio Corporation of America (RCA) procedure. Then, Fe film was evaporated onto the silicon substrate as the catalyst metal. The thickness of Fe film was 10nm which was precisely controlled with a thickness monitor. Substrates with Fe film were mounted on a ceramic holder, and put into a quartz furnace to be preheated in an atmosphere of Ar at 900°C for 10min. The purpose of preheat treatment is to form nano-sized Fe particles which determine the diameter of synthesized CNTs. A mixture of methane (CH₄) and argon (Ar) are subsequently fed into the furnace to synthesize CNTs. The flow rates of CH₄ and Ar during the growth of CNTs were 100sccm and 1800sccm, respectively. The temperature was set to 900°C, and the growth time is 15min.

B. Sensing Measurement

Gas-sensing experiments were carried out by an ultrahigh vacuum measurement system shown in Fig. 1. It was set up by four basic components: vacuum chamber, Keithley 237 measurement system, pumping system, and Mass Flow Control (MFC) controller system. The pumping system consists of a machine pump and a magnetic-levitated turbo pump. The pressure of chamber can be extract to an ultrahigh vacuum environment of 10⁻⁷ Torr by using a magnetic-levitated turbo pump. The prototype CNTs sensor was then exposed to different chamber pressure of ethanol vapors ranging from 50m to 50Torr. The I-V traces and resistance of the carbon nanotubes were measurement by the Keithley 237 current-voltage analyzer and two-probe method using Ag electrodes.



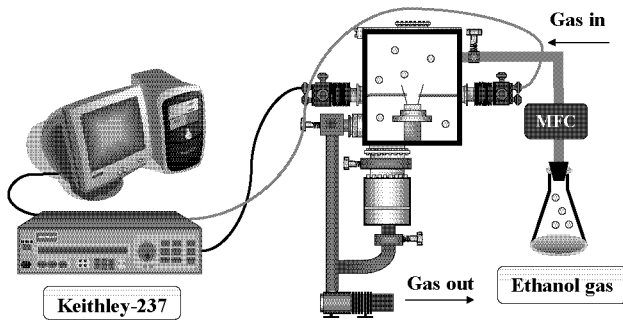


Fig. 1. Schematic diagram of the experimental setup.

III. RESULTS AND DISCUSSION

Figure 2(a) shows the top view of SEM images of as-grown, unexposed CNTs are randomly oriented, smooth, and tidy. Figure 2(b) shows the emission current density plotted against the applied field (J - E) characteristics of the CNTs sensor before any exposure to ethanol which exhibit diode behavior at room temperature with drastic current changes can carry large current of up to 1.2 mA/cm^2 at $4.8 \text{ V}/\mu\text{m}$. The field emission tests indicated an extremely low turn-on field of $\sim 3 \text{ V}/\mu\text{m}$ indicating that CNTs are excellent field emitters and have potential for low field displays. In Fig. 2(b), five curves (J1 through J5) were plotted basically reproducible, but slight disturbance was observed due to the imperfect connection between the carbon nanotube and electrodes. The successful utilization of carbon nanotubes in gas sensors may open a new door for the development of superior microelectronic gas sensors.

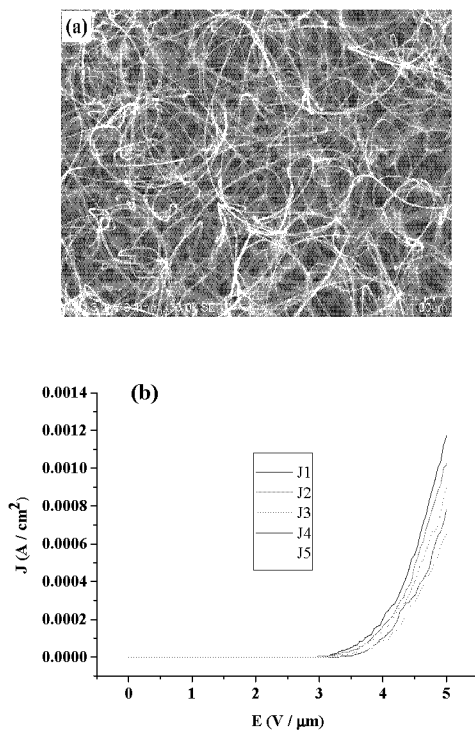


Fig. 2. (a) SEM micrograph of as-grown, unexposed CNTs (b) Room temperature J - E characteristics of the unexposed CNTs sensor.

XPS technique was used to analyze the surface chemical composition of the CNTs. From Fig. 3, the ratio of the oxygen to carbon (O/C) signal intensity was 0.094 for the unexposed CNTs. The high resolution C_{1s} core-levels were recorded to analyze chemical-binding species on the unexposed CNTs surface in detail. In this study, the concentration of each element was calculated from the peak area obtained by a best-fit Gaussian computer program. The binding energy of each element was determined at the center position of its XPS peak. The C_{1s} spectrum of unexposed CNTs shown in Fig. 3, the functionalized groups for four core-level peaks at 284.6, 286.2, 288.2 and 289.0 eV are assigned to the C-C, C-O, C=O and O-C=O bonds respectively. It was the most powerful evidence to demonstrate that oxygen atom was doped into the surface of CNTs.

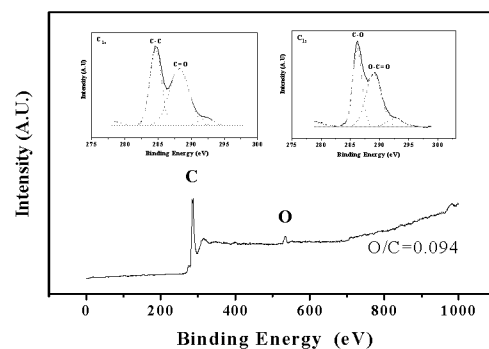


Fig. 3. XPS characterization of MWNTs.

Figure 4(a) shows the relative resistance response of the sensor towards various chamber pressure levels of ethanol vapors. Upon an ethanol filling and pumping environment, fig. 4(a) clearly shows a significant increase in the resistance response towards increasing chamber pressure levels of ethanol vapors from 50m to 50 Torr. The resistance responses were also found to be reversible and consistent. All experiments were conducted at room temperature. Fig. 4(b) shows the relation between sensitivity and an ethanol filling pressure. The scale of X-axis is \log_{10} . The sensitivity (relative resistance response) is defined as $(R-R_0)/R_0$ where R is the resistance of the sensor when the vapor to be sensed is introduced and R_0 is the resistance of the sensor in air [7-9]. It was found that the higher chamber pressure exhibited higher sensitivity than lower ones, and the trend was more obvious under a higher ethanol pressure. It is evident that the sensing responses increase with the increment of the gas pressure and the sensor exhibits a fast response and a good recovery. The underlying principle can be explained on the basis of the sensing mechanism based on the hydrogen bonding of the functionalized groups on CNTs with adsorbed molecules as reported by Sin et al. [11]. This neutralizes the free charge carriers- holes of the p-type CNTs thus increasing its electrical resistance upon ethanol exposure.

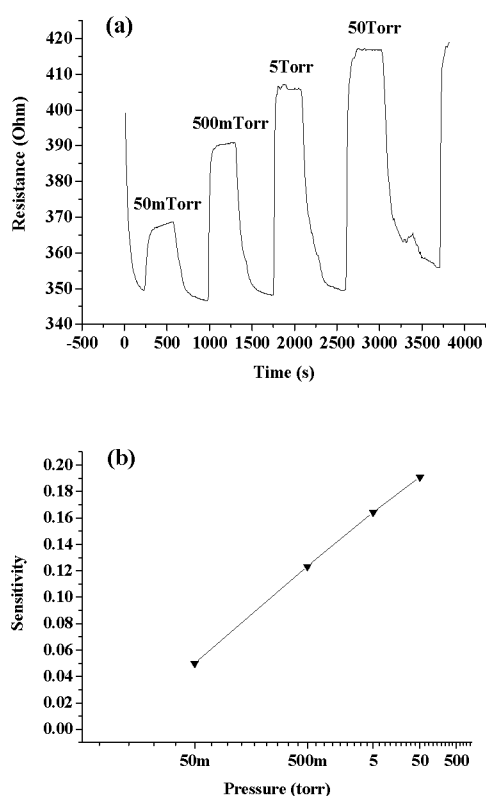


Fig. 4. (a) Sensor response towards different chamber pressure of ethanol vapors. (b) The relation between sensitivity and an ethanol filling pressure. (X-axis: log10)

IV. CONCLUSION

Carbon nanotubes were synthesized by thermal chemical vapor deposition (thermal CVD) at 900°C under CH_4 gas flow rate of 100sccm. We have studied the room temperature performance of a CNT-based prototype sensor towards ethanol. Upon exposure to a with and without ethanol environment at the room temperature of 25°C , the electrical resistance of as-grown devices was found to increase and to return back respectively. It showed a significant and sharp increase in resistance response even for ethanol vapor chamber pressure as low as 50mTorr. Furthermore, the device became more sensitive for ethanol detection by applying a high chamber pressure. Based on our experimental results, it was concluded that the alteration of free holes concentration in the CNT's mat played the major mechanism for the ethanol gas detection. The CNT-based sensor described here has a potential for commercialization because of its simple and low cost fabrication process.

V. REFERENCES

- [1] Y. Wang, and J.T.W. Yeow, "A review of carbon nanotubes-based gas sensors," *Journal of Sensors*, vol. 2009, pp. 493904-493928, 2009.
- [2] F. Villalpando-Páez, A.H. Romero, E. Muñoz-Sandoval, L.M. Martínez, H. Terrones, and M. Terrones, "Fabrication of vapor and gas sensors using films of aligned CNx nanotubes," *Chemical Physics Letters*, vol. 386, pp. 137-143, 2004.

- [3] S. Chopra, K. McGuire, N. Gothard, A.M. Rao, and A. Pham, "Selective gas detection using a carbon nanotube sensor," *Appl. Phys. Lett.*, vol. 83, pp. 2280-2282, 2003.
- [4] Philip G. Collins, Keith. Bradley, Masa. Ishigami, and A. Zettl, "Extreme Oxygen Sensitivity of Electronic Properties of Carbon Nanotubes," *SCIENCE*, vol. 287, no. 5459, pp. 1801-1804, 2000.
- [5] Jing. Kong, Nathan R. Franklin, Chongwu. Zhou, Michael G. Chapline, Shu. Peng, Kyeongjae.Cho, and Hongjie. Dai, "Nanotube Molecular Wires as Chemical Sensors," *SCIENCE*, vol. 287, no. 5453, pp. 622-625, 2000.
- [6] H. Haspel, R. Ionescu, P. Heszler, A. Kukovecz, Z. Kónya, Z. Gingl, J. Máklin, T. Mustonen, K. Kordás, R. Vajtai, and P.M. Ajayan, "Fluctuation enhanced gas sensing on functionalized carbon nanotube thin films," *Physica Status Solidi (b)*, vol. 245, no. 10, pp. 2339-2342, 2008.
- [7] B. Philip, J.K. Abraham, A. Chandrasekhar, and V.K. Varadan, "Carbon nanotube/PMMA composite thin films for gas-sensing applications," *Smart Materials and Structures*, vol. 12, no. 6, pp. 935-939, 2003.
- [8] S. Rajaputra, R. Mangu, P. Clore, and Vijay P. Singh, "Multi-walled carbon nanotube arrays for gas sensing applications," *Nanotechnology*, vol. 19, no. 34, pp. 345502-345508, 2008.
- [9] S. Yun, and J. Kim, "Multi-walled carbon nanotubes cellulose paper for a chemical vaporsensor," *Sensors and Actuators B*, vol. 150, no. 1, pp. 308-313, 2010.
- [10] Y. Zhang, T.F. Kang, Y.W. Wan, and S.Y. Chen, "Gold nanoparticles-carbon nanotubes modified sensor for electrochemical determination of organophosphate pesticides," *Microchimica Acta*, vol. 165, no. 3-4, pp. 307-311, 2009.
- [11] M.L.Y. Sin, G.C.T. Chow, G.M.K. Wong, W.J. Li, P.H.W. Leong, and K.W. Wong, "Ultralow-power alcohol vapor sensors using chemically functionalized multiwalled carbon nanotubes," *IEEE Transactions on Nanotechnology*, vol. 6, no. 5, pp. 571-577, 2007.

BIOGRAPHY



Chun-Shin Yeh received the Ph.D. from National Yunlin University of Science and Technology, Yunlin, Taiwan, in 2009. He is currently an associate professor at department of Electronic Engineering, Chienkuo Technology University. His main research interests are diamond films, carbon nanotubes, and nano technology.

