MWCNT Thin Films by CVD Method and Some Applications

Intessar K. Abd[1], Ahmed M. Shano[2,*], Ziad T. Khodair[3]

[1] *College of Education for Pure Science, Diyala University, Diyala, Iraq*
[2] *Department of Radiolgical Tech., Bilad Alrafidain University Collage, Diyala, Iraq*
[3] *University of Diyala, College of Science, Department of Physics, Diyala, Iraq*

(Received 03 October 2022; revised manuscript received 19 December 2022; published online 27 December 2022)

Chemical Vapor Deposition (CVD) is employed in this study to create MWCNT thin films. The examination of X-ray diffraction (XRD) shows that there are several strong peaks at $2\theta \sim 35.5°$, 54°, 57°and 62° which are attributed to the (222), (004), (104) and (015) planes, respectively. This leads to the conclusion that the sample is polycrystalline in nature with a hexagonal crystalline structure. The Field Emission Scanning Electron Microscope (FE-SEM) images highlight the shape of CNTs produced on catalyst particles using the CVD process. MWCNTs are synthesized in a variety of forms, including straight arrangement, branching arrangement, coil MWCNT structures, curly and helical-shaped structures. A reduced sensor is conceivable; this could result in a sensor that is lighter, cheaper and consumes less power. A MWCNT thin film is fabricated as a gas sensor based on glass substrates, where CH_4 and CO_2 gases with concentrations of 1, 2, 3 and 4 ppm are examined, and this study is conducted to see how the absorption of CH_4 and CO_2 gases affects the change in the resistance of CNT pellets. According to the study, CNTs are highly sensitive to gases like CH_4 and CO_2. Future research into CNT-based sensors is expected to focus on a wide range of applications as the interest of the nanotechnology research community in this area grows.

Keywords: MWCNTs, Thin films, CVD method, Structural properties, Sensitivity.

DOI: 10.21272/jnep.14(6).06002 PACS numbers: 81.15.Gh, 81.40.Vw

1. INTRODUCTION

Carbon nanotubes (CNTs) are tubular forms of carbon with diameters as tiny as 1 nm and lengths ranging from a few nm to microns. CNT is a two-dimensional graphene sheet folded into a tube in terms of the arrangement. It has Young's modulus of over 1 TPa and tensile strength of 200 GPa. The electronic properties of CNTs can be metallic or semiconducting depending on the atomic arrangement of carbon atoms that make up a nanotube (chirality), making them widely used in a variety of applications such as solar cells, fuel cells, supercapacitors, transistors, memories, displays, filters, purification systems, sensors, etc. due to their unique electrical, mechanical, optical, thermal, and other properties [1, 2]. Chemical vapor deposition (CVD) was used to make CNTs. The most frequent approach for growing CNT thin films directly is CVD. Catalyst nanoparticles on substrates are employed as seeds for CNT development in the CVD process [3-6]. The hydrocarbon carrier gas, growth time and temperature, and catalyst composition are the essential parameters that influence the growth kinetics. Although vertically oriented CNTs have unique features and device applications, such as in-field emission devices and super capacitors, patterned catalysts, electric or magnetic fields during the CVD process, directional gas flow, or the use of a substrate with a predetermined lattice structure can all be used to create aligned CNT films [6, 7]. As the film thickness grows, CNT thin films demonstrate a semiconductor-metal transition and can be employed as the active layer in thin-film transistors and sensors [8, 9]. Films with thicknesses ranging from 10 to 100 nm have good optical transparency and electrical conductivity, making them a viable alternative to ITO electrodes. CNT films that are micrometer thick and nanoporous are employed as electrodes in supercapacitors, fuel cells, and batteries [10]. In this work, CNT thin films were synthesized at 700 °C by CVD from a methanol/butanol mixture by using ferrocene as a growth catalyst.

2. EXPERIMENTAL PART

The production method employed in this study is CVD. Methanol and butanol were used as a hydrocarbon source with nitrogen as carrier and purge gas. The reaction temperature is in the range of 650-700 °C, while the reaction time is 30 min. In a typical experiment, we put a quartz substrate (1 cm × 1 cm) that was placed in a ceramic boat in a furnace. At first, the ceramic tube was flushed with nitrogen to eliminate oxygen from the reaction chamber while heating the reactor. When the furnace reached a temperature of 700 °C, N_2 carrier flow (150 ml/min) was bubbled into the (C1/C4) mixture (50 ml) used as a hydrocarbon source. Then, (C1/C4) mixture was decomposed in the furnace to form CNTs. The reaction was over after 30 min and the furnace was cooled down with N_2 flow. In order for synthetic CNTs to react with a gas sensor, we should place CNTs on the surface and use measurements of the electrical characteristics of the samples while they are exposed to gases. We examined the current-time (*I*-*t*) response both

* dr.ahmed.alaskari89@gmail.com

before and during gas exposure to study the electrical properties. To deposit samples on the substrate, 10 mg of the powder were poured into 100 ml of ethanol and then sonicated for 15 min with a power of 75 W. At the next step, we deposited the material on the substrate by the drop-casting method. After that, we put the samples at room temperature for a day to dry.

3. RESULTS AND DISCUSSION

Fig. 1 shows the X-ray spectra for CNT thin films. Several peaks are observed there, the strong peaks at $2\theta \sim 35.5°$, 54°, 57°and 62° are attributed to the (222), (004), (104) and (015) planes, respectively, of the Fe substrate which was used as a catalyst for the precipitation method. The positions of the peaks and the presence of more than one diffraction peak lead to the conclusion that the samples are polycrystalline in nature with a hexagonal crystalline structure [11]. Fig. 1 shows images taken with a Field Emission Scanning Electron Microscope (FE-SEM) that highlight the shape of CNTs produced on catalyst particles using the CVD process. MWCNTs were synthesized in various forms, including straight arrangement, branched arrangement, coil MWCNT structures, curly and helical structures, which is consistent with [12].

3.1 MWCNT Thin Film on Glass Gas Sensor

A MWCNT thin film was fabricated as a gas sensor based on glass substrates, where CH_4 and CO_2 gases with concentrations of 1, 2, 3 and 4 ppm were studied. Fig. 2 and Fig. 3 show the sensitivity as a function of gas concentration with and without exposure to the examined gasses for MWCNT thin films at different operating temperatures (room temperature, 50, 70 and 100 °C) with respect to CH_4 and CO_2 gases. The gas sensitivity was calculated according to the equation [13-15]:

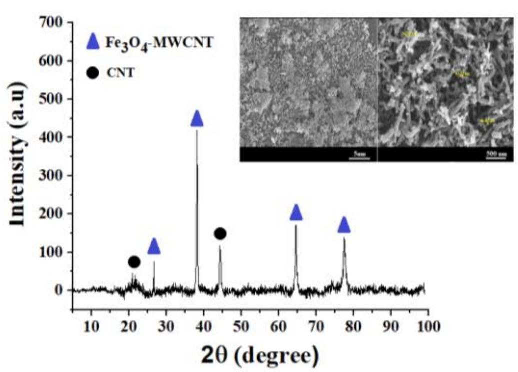

Fig. 1 – XRD of MWCNTs obtained at 700 ºC

$$s = \left| \frac{R_g - Ra}{R_a} \right| \times 100\% , \qquad (1)$$

where R_a and R_g are the sample resistances exposed to a clean air and gas-air mixture. Fig. 2 shows the variation of the CH_4 gas sensitivity vs the operating temperature for MWCNT thin films at different temperatures. The maximum sensitivity appeared in the sample at 70 °C by gaining electrons from n-type samples and a decrease in their resistance by reducing gasses adsorbed on the gas sensor surface. In keeping with the findings of Ato et al. [16] and Deshpande et al. [17], the sample resistance decreases exponentially when exposed to CH_4 gas due to an increase in the majority charge carrier concentration in the conduction band. While CO_2 gas absorbs more electrons from the sample surface, the increase in sample resistance is the result of a decrease in the concentration of electrons near the surface of the n-type semiconductor. Due to the high surface-to-volume ratio, the nanoparticle size has a significant impact on sensitivity [18, 19]. Fig. 2 shows that the sensitivity of the membrane to CH_4 gas increases with an increase in the gas concentration as well as with an increase in the operating temperature.

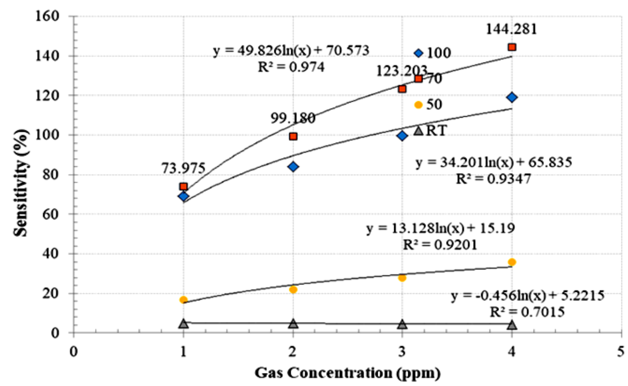

Fig. 2 – CH_4 gas sensitivity for MWCNT films at different temperatures

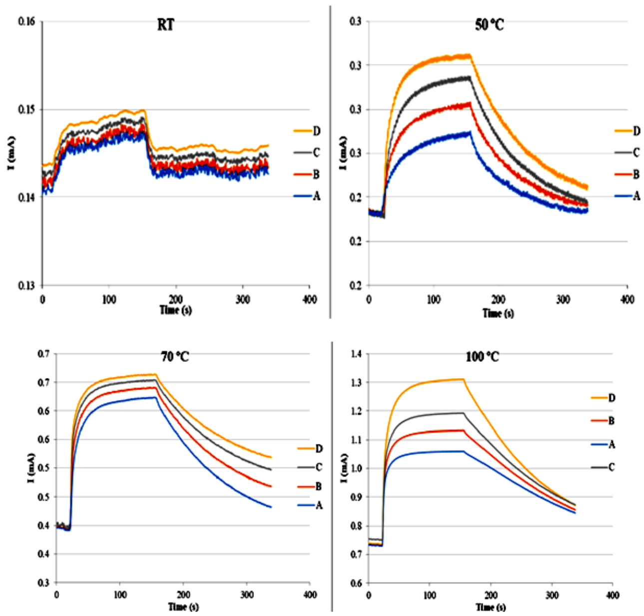

Fig. 3 – Current variation for MWCNT films with different concentrations and different operating temperatures with respect to CH_4 gas

The reason is due to the decrease in the thermal energy of gas molecules interacting with oxygen molecules adsorbed on the surface, and that the type of this adsorption of oxygen molecules is chemisorption, which occurs when the temperature of the membrane increases [20]. We notice from Fig. 3 that the current values increase under the action of the reducing CH_4 gas, since the oxygen ions adsorbed on the surface of the membrane decrease. Then the concentration of charge carriers (electrons) on both sides of the voltage barrier increases, so the barrier growth decreases and the resistance decreases, so the carriers can cross the voltage barrier and the conductivity increases. The operating temperature of 100 °C is due to an increase in the homogeneity of the membrane surface with a uniform roughness, providing a large area. This leads to an increase in the interaction of the gas with the membrane surface [12, 20].

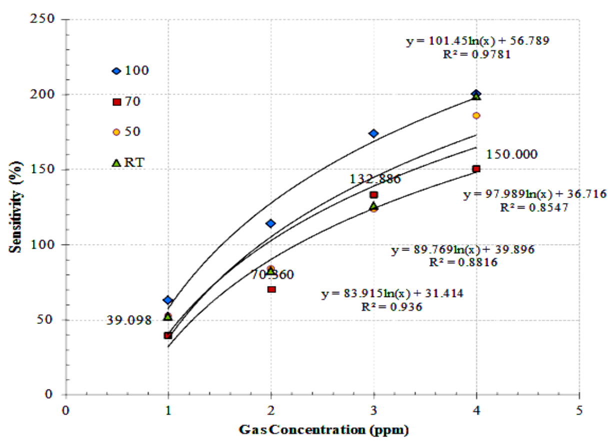

Fig. 4 – CO_2 gas sensitivity for MWCNT films on glass substrates at different temperatures

From Fig. 4, we notice an increase in the sensitivity of the membrane when exposed to a reducing gas with an increase in the operating temperature, as well as its increase with an increase in gas concentration. Due to a decrease in the thermal energy CO_2 molecules interact with oxygen molecules adsorbed on the surface [26]. It can be seen from Fig. 5 that the current values decrease when the membrane is exposed to the oxidizing CO_2 gas, since the number of oxygen ions adsorbed on the surface at the grain boundaries with gas molecules increases.

Then the concentration of most charge carriers (electrons) on both sides of the voltage barrier decreases, so barrier growth increases and the resistance increases, which prevents carriers from crossing the barrier. The conductivity decreased and amounted to the lowest current value at the operating temperature (100 °C).

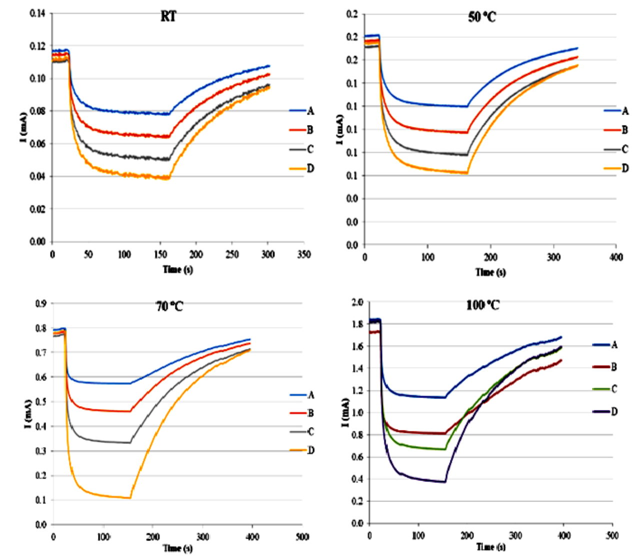

Fig. 5 – Current variation for MWCNT thin films at different operating temperatures with respect to CO_2 gas

4. CONCLUSIONS

The experimental findings have shown that CNTs are capable of sensing methane gas and carbon dioxide at ambient temperatures. As a result, it can be said that the analysis of gas sensing properties has demonstrated that CNTs can potentially be good materials for methane gas and carbon dioxide sensor materials at room temperature. We conclude from this work that the type and concentration of the gas used affected the sensitivity of the membrane as well as the operating temperature, and the sensitivity of the film to carbon dioxide was better than the sensitivity of the film to methane gas at the same concentration.

REFERENCES

1. J. Prasek, J. Drbohlavova, J. Chomoucka, J. Hubalek, O. Jasek, V. Adam, R. Kizek, *J. Mater. Chem.* **21** No 40, 15872 (2011).
2. R. Purohit, K. Purohit, S. Rana, R.S. Rana, V. Patel, *Procedia Mater. Sci.* **6**, 716 (2014).
3. B.H. Chen, H.C. Lin, T.Y. Huang, J.H. Wei, H.H. Wang, M.J. Tsai, T.S. Chao, *Appl. Phys. Lett.* **88** No 9, 093502 (2006).
4. I.K. Abd, A.M. Shano, E.K. Alwan, *J. Nano- Electron. Phys.* **14** No 3, 03024 (2022).
5. Z.T. Khodiar, N.F. Habubi, A.K. Abd, A.M. Shano, *Int. J. Nanoelectron. Mater.* **13** No 3, 433 (2020).
6. A.M. Khudhur, A.M. Shano, A.S.H. Abbas, *J. Phys. Conf. Ser.* **1999** No 1, 012127 (2021).
7. D.N. Futaba, K. Hata, T. Yamada, T. Hiraoka, Y. Hayamizu, Y. Kakudate, S. Iijima, *Nat. Mater.* **5** No 12, 987 (2006).
8. A.M. Shano, I.M. Ali, NA. Bakr, *J. Nano- Electron. Phys.* **11** No 6, 06016 (2019).
9. A.M. Shano, Z.S. Ali, *J. Nano- Electron. Phys.* **12** No 4, 04001 (2020).
10. H.E. Unalan, G. Fanchini, A. Kanwal, A. Du Pasquier, M. Chhowalla, *Nano Lett.* **6** No 4, 677 (2006).
11. R. Siddheswaran, D. Manikandan, R.E. Avila, C.E. Jeyanthi, R.V. Mangalaraja, *Fuller. Nanotub. Carbon Nanostruct.* **23** No 5, 392 (2015).
12. L. Liao, Z. Zhang, B. Yan, Z. Zheng, Q.L. Bao, T. Wu, T. Yu,

J. Nanotechnol. **20** No 8, 085203 (2009).
13. Z.T. Khodair, M.A. Al-Jubbori, A.M. Shano, F.I. Sharrad, *Chem. Data Collect.* **28**, 100414 (2020).
14. Z.S. Ali, A.M. Shano, *J. Electron. Mater.* **49**, 5528 (2020).
15. I.M. Ali, A.M. Shano, N.A. Bakr, *J. Mater. Sci.: Mater. Electron. Mater.* **29** No 13, 11208 (2018).
16. K. Kato, N. Watanabe, S. Katagiri, K. Shinbo, F. Kaneko, J. Locklin, R.C. Advincula, *Jpn. J. Appl. Phys.* **43** No 4S, 2311 (2004).
17. S. Radhakrishnan, S.D. Deshpande, *Sensors* **2** No 5, 185 (2002).
18. J.C. Hsieh, C.J. Liu, Y.H. Ju, *Thin Solid Films* **322** No 2, 98 (1998).
19. J.R. Nataraj, P.Y. Bagali, M. Krishna, M.N. Vijayakumar, *Mater. Today: Proc.* **5** No 4, 10670 (2018).
20. J. Mathiyan, D. Sivalingam, J.B. Gopalakris, J.B.B. Rayappan, *J. Appl. Sci.* **12** No 16, 1686 (2012).

Тонкі плівки на основі MWCNT, отримані методом CVD, та деякі їх застосування

Intessar K. Abd[1], Ahmed M. Shano[2], Ziad T. Khodair[3]

[1] *College of Education for Pure Science, Diyala University, Diyala, Iraq*
[2] *Department of Radiolgical Tech., Bilad Alrafidain University Collage, Diyala, Iraq*
[3] *University of Diyala, College of Science, Department of Physics, Diyala, Iraq*

Хімічне осадження з парової фази (CVD) використовується в цьому дослідженні для створення тонких плівок на основі MWCNTs. Дослідження методом рентгенівської дифракції (XRD) показує, що є кілька сильних піків при $2\theta \sim 35{,}5°$; 54°; 57° і 62°, які відносять відповідно до площин (222), (004), (104) і (015). Це дозволяє зробити висновок, що зразок є полікристалічним за своєю природою з гексагональною кристалічною структурою. Зображення скануючого електронного мікроскопа з польовою емісією (FE-SEM) підкреслюють форму CNTs, отриманих на частинках каталізатора за допомогою процесу CVD. MWCNTs синтезуються в різноманітних формах, у тому числі з прямим розташуванням, розгалуженням, котушковими структурами на основі MWCNT, фігурними та спіральними структурами. Можливий зменшений датчик; це може призвести до того, що датчик буде легшим, дешевшим і споживатиме менше енергії. Тонка плівка на основі MWCNT виготовляється як датчик газу на скляних підкладках, де досліджуються гази CH_4 і CO_2 з концентраціями 1, 2, 3 і 4 ppm, і це дослідження проводиться, щоб побачити, як поглинання газів CH_4 і CO_2 впливає на зміну опору гранул CNTs. Згідно з дослідженням, CNTs дуже чутливі до таких газів, як CH_4 і CO_2. Очікується, що майбутні дослідження датчиків на основі CNTs будуть зосереджені на широкому діапазоні застосувань, оскільки інтерес дослідницького співтовариства нанотехнологій до цієї галузі зростає.

Ключові слова: MWCNTs, Тонкі плівки, Метод CVD, Структурні властивості, Чутливість.