Journal of Nano- and Electronic Physics
Vol. **11** No 5, 05015(4pp) (2019)

Журнал нано- та електронної фізики
Том **11** № 5, 05015(4cc) (2019)

Functionalized Carbon Nanotubes on Porous Silicon for Sensing Application

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(Received 23 June 2019; revised manuscript received 08 October 2019; published online 25 October 2019)

The evolution of carbon nanotube (CNTs) based gas sensors has attracted great interest among researchers in the last decade because of their selectivity for various gaseous media, fast response, high sensitivity and room temperature operation. Functionalized single-walled carbon nanotubes (F-SWCNTs) and functionalized multi-walled carbon nanotubes (F-MWCNTs) have been utilized to manufacture nitrogen dioxide gas sensor. CNTs films have been deposited on (*n*-type) porous silicon substrate by the drop casting technique. A porous silicon layer (PS) was prepared using the photo-electrochemical etching. The applied current density is 20 mA/cm^2 with green laser radiation, and the typical photo-electrochemical etching time was about 15 min. When the F-SWCNTs and F-MWCNTs samples were exposed to NO_2 gas at different operating temperatures, the sensitivity response results show that the F-SWCNTs have better performance than the F-MWCNTs. At 200 °C the F-SWCNTs/PS sensitivity reaches 61%, the response time and the recovery time were about 10 s and 214 s, respectively; whereas for the F-MWCNTs/PS the sensitivity reaches 57 % at 100 °C, the response time and the recovery time were about 20 s and 647 s, respectively. At the same time, the F-MWCNTs have an operating temperature (100 °C) less than that of the F-SWCNTs (200 °C).

Keywords: F-SWCNTs, F-MWCNTs, Oxidizing gas, Sensitivity, Response time, Porous silicon.

DOI: 10.21272/jnep.11(5).05015 PACS number: 61.48.De

1. INTRODUCTION

Since the discovery, carbon nanotubes (CNTs) have been extensively studied due to their unique properties as a perfect one-dimensional material [1]. CNTs have extremely special properties, because of their hole structure, nanometer size, high surface to volume ratio, and can change their electrical resistance drastically when exposed to different gases at room temperature [2]. Sensors manufactured with CNTs have been observed to be very sensitive to surrounding gases, owing to their properties such as fast response and high sensitivity [3]. Alteration of CNTs with different functional groups changes their electronic property, in this manner improving their selectivity and expanding their reaction towards specific gases. The CNTs change with a carboxylic group. The carboxylic group will make reactive sites at the sidewalls and end of the CNTs where active interaction with target atoms occurs [4].

A high surface to volume proportion makes porous silicon to be a very attractive contender for gas, chemical and organic sensors. In correlation with different nanomaterials with high surface to volume ratio porous Si has priority of variable pores and interconnects sizes. This may give a higher scope of synthetic compounds which can be detected [5, 6]. The present work makes a comparison between the sensing performance of the functionalized single-walled CNTs (F-SWCNTs) and functionalized multi-walled CNTs (F-MWCNTs) as NO_2 gas sensor deposited on porous silicon.

2. EXPERIMENTAL

In this work, 1.5×1.5 cm^2 dimensions primary n-type silicon wafer substrates were thoroughly cleaned to decontaminate their surface from any available dirt. A porous silicon layer (PS) was prepared via photo-electrochemical etching. This process was carried out by immersing the samples in HF acid of 40 % concentration mixed with ethanol in 1:1 ratio in a Teflon beaker. The applied current density was 20 mA/cm^2 with a green laser source, and the typical photo-electrochemical etching time was chosen to be about 15 min. CNTs used in this research were purchased from the Nanostructured & Amorphous Materials, Inc. (USA); for F-SWCNTs (purity > 90 wt. %; weight 1 g; OD 1-2 nm; length ~ 30 μm; COOH content 2.73 wt. %; Ash < 1.5 wt. %; SSA 380 m^2/g) and for F-MWCNTs (purity > 95 wt. %; weight 5 g; OD 20-30 nm, length ~ 30 μm, COOH content 1.23 wt. %; Ash < 1.5 wt. %; SSA 110 m^2/g).

To prepare F-SWCNTs sample, 0.03 g of CNTs were dispersed in dimethylformamide (DMF). A magnetic stirrer was incorporated for this purpose for 1 hour, followed by 2 hour sonication. The obtained solution was used for film deposition on porous silicon by the drop casting method. To prepare F-MWCNT sample, 0.05 g of CNTs were dispersed in DMF. A magnetic stirrer was incorporated for this purpose for 1 hour, followed by 2 hour sonication. The obtained solution was used for film deposition on porous silicon by the drop casting method.

3. RESULTS AND DISCUSSION

The sensor response (S) is defined as the ratio of the change in resistance ($R_g - R_a$) upon exposure to target analyte to the resistance (R_a) of the sensor in air

$$S = \left| \frac{R_{air} - R_{gas}}{R_{gas}} \right| \cdot 100\%,$$

where R_g and R_a are the resistances of the sensor in the presence of NO_2 and in air respectively.

The response time and recovery time were calculated as the time taken for the sensor to attain 90 % of total resistance change (t_{90}) from its initial resistance [7].

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3.1 Sensing Characteristics of F-SWCNTs on Porous Silicon

The sensor working principle is adsorption of electron donating (NO_2) on the CNT surface result in charge transfer between the CNT and gas molecules [8]. Fig. 1 shows the variation of resistance as a function of time. Experimental results indicated an increase in conductance of CNTs when exposed to oxidizing gases like NO_2. This behavior may be attributed to the charge transfer occurring from CNTs to NO_2 because of its highly oxidizing nature. When oxidizing gases like NO_2 are adsorbed on the surface of p-type CNTs, the Fermi levels are shifted towards the valence band, generating more holes and thus enhancing conductance [9]. The response and recovery times of F-SWCNTs gas sensor were respectively 10 s and 214 s at 200 °C.

3.2 Sensing Characteristics of F-MWCNTs on Porous Silicon

Fig. 2 shows the variation of resistance as a function of time. Experimental results indicated an increase in conductance of CNTs when exposed to oxidizing gases like NO_2. This behavior may be attributed to the charge transfer occurring from CNTs to NO_2 because of its highly oxidizing nature.

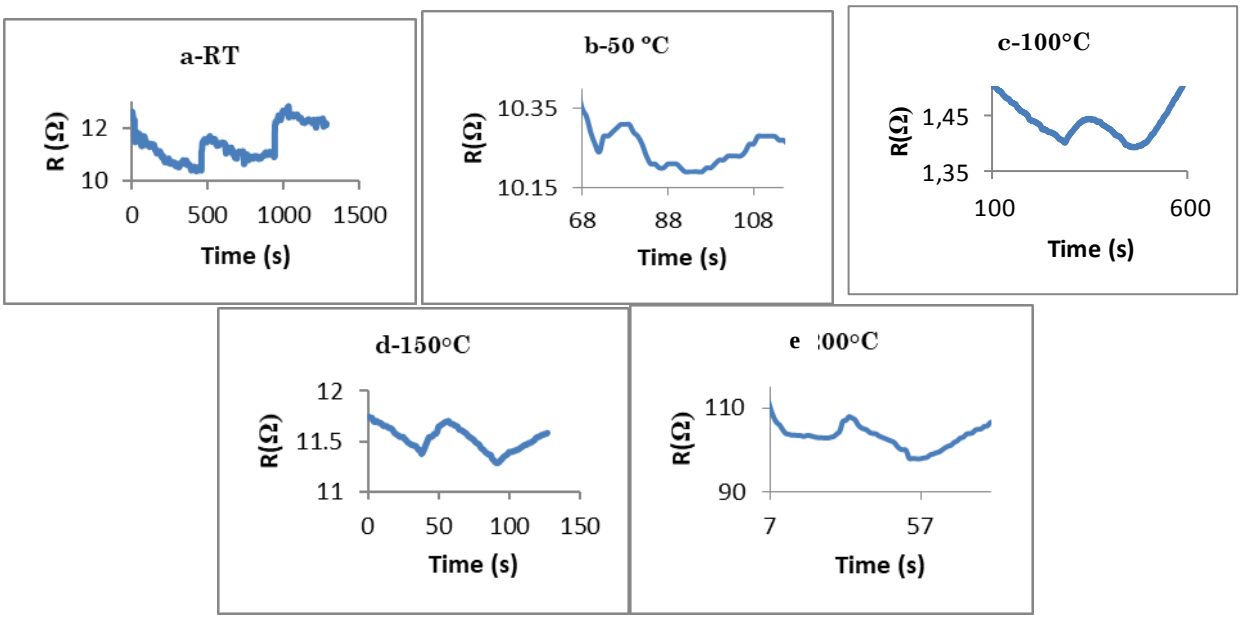

Fig. 1 – Resistance-time variation of F-SWCNTs sensor time at RT (a), 50 (b), 100 (c), 150 (d) and 200 (e) testing temperature upon exposure to NO_2 gas

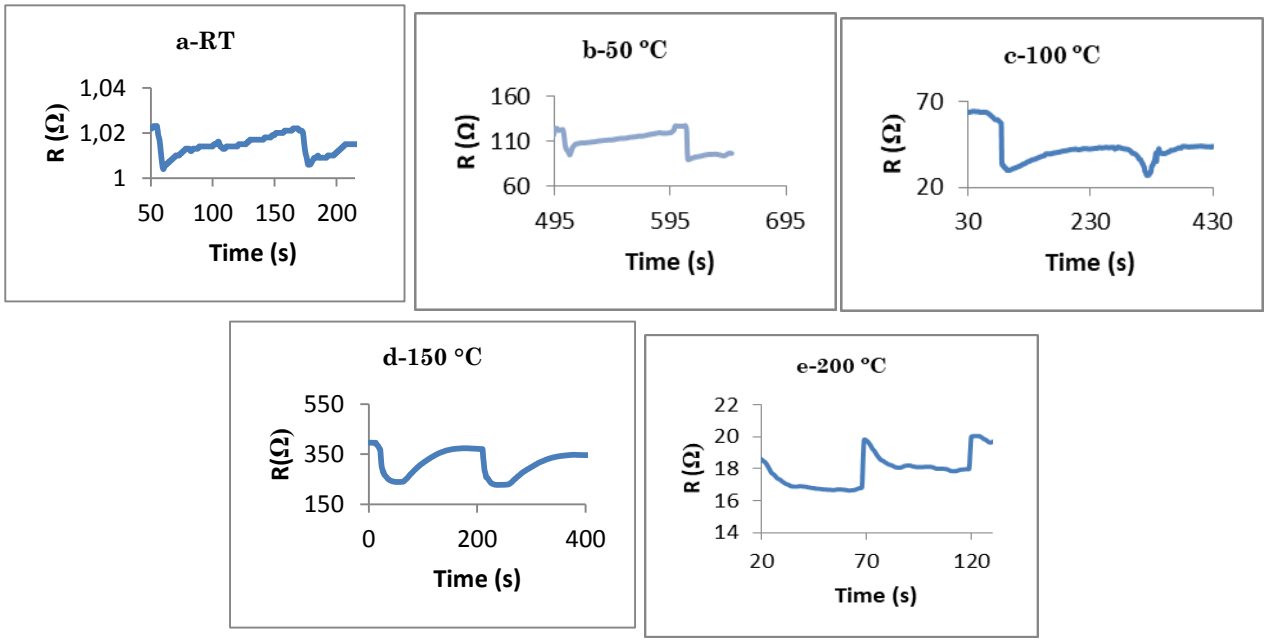

Fig. 2 – Resistance-time variation of F-MWCNTs sensor time at RT (a), 50 (b), 100 (c), 150 (d) and 200 (e) testing temperature upon exposure to NO_2 gas

Table 1 – The sensitivity, response and recovery time of the F-SWCNTs/PS thin film upon exposure to NO_2 gas at different temperatures

Type	T,°C	S, %	t_s, s	t_c, s
F-SWCNTs/PS	RT	23	4	33
	50	11.1	6	142
	100	15	22	653
	150	42	12	346
	200	61	10	214

Table 2 – The sensitivity, response and recovery time of the F-MWCNTs/PS thin film upon exposure to NO_2 gas at different temperatures

Type	T,°C	S, %	t_s, s	t_c, s
F-MWCNTs/PS	RT	4.2	12	261
	50	36	9	213
	100	57	17	647
	150	43	26	287
	200	45	20	146

The response and recovery times of F-MWCNTs gas sensor were respectively 17 s and 647 s at 100 °C. By the comparison between Table 1 and Table 2, it can be seen that the maximum sensitivity of F-SWCNTs is 61 % at operating temperature 200 °C which is higher than the sensitivity of F-MWCNTs which is 57 % at operating temperature 100 °C. But at the same time, F-MWCNTs have operating temperature less than F-SWCNTs. This can be attributed to the functionalization of CNTs by adding the carboxyl group –COOH. Use of functionalized CNTs will provide open side wall due to oxidative damage to the nanotube framework by strong acids, which leave holes functionalized with oxygenated functional groups (–COOH). This treatment of CNTs with strong acids tends to open these tubes, which increase the adsorption of the gas in the CNTs wall and increase the sensitivity. They are also attributed for deposits of CNTs on porous silicon because porous silicon has large surface to volume ratio, which in turn will cause more dispersion of the CNTs and thus increasing the surface to volume ratio of interaction between CNTs and NO_2 gas.

4. CONCLUSIONS

Gas sensing property analysis of the F-SWCNT and F-MWCNTs based gas sensors on porous silicon prepared using the photo-electrochemical etching revealed a good sensor performance for F-SWCNTs/PS and F-MWCNT/PS for NO_2 gas, which is attributed to the presence of functionalization of CNTs by adding the carboxyl group (–COOH) to SWCNT and MWCNTs and also attributed for deposits of CNTs on porous silicon because porous silicon has large surface to volume ratio, which in turn will cause more dispersion of the CNTs and thus increasing the surface to volume ratio of interaction between CNTs and NO_2 gas. The F-CNTs sensor has proved highly efficient in use as a sensor to detect NO_2 gas since functionalized CNTs will provide open side wall due to oxidative damage to the nanotube framework by strong acids, which leave holes functionalized with oxygenated functional groups (–COOH). This treatment of CNTs will increase the adsorption of the gas in the CNTs wall and increase the sensitivity.

In the present work, results obtained have shown fast response and good reversibility for the F-SWCNTs/PS (response time 10 s and recovery time 214 s at 200 °C) based sensor compared to the F-MWCNTs (response time 17 s and recovery time 647 s at 100 °C) which can be mainly attributed to the enhanced charge transfer through F-SWCNTs. The F-SWCNTs/PS nanocomposite was found to be highly selective towards NO_2 gas. The sensor response could be optimized by varying the porosity of the layer, since the electrical response is essentially conditioned by specific surface of material.

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Функціоналізовані вуглецеві нанотрубки на поруватому кремнії для сенсорних застосувань

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Еволюція газових датчиків на основі вуглецевих нанотрубок (CNTs) викликала великий інтерес серед дослідників в останнє десятиріччя через їх вибірковість для різних газоподібних середовищ, швидку реакцію, високу чутливість та роботу за кімнатної температури. Функціоналізовані одностінні

вуглецеві нанотрубки (F-SWCNTs) та функціоналізовані багатостінні вуглецеві нанотрубки (F-MWCNTs) були використані для виготовлення датчика газу на основі діоксиду азоту. Плівки з CNTs наносилися на порувату підкладку кремнію (*n*-типу) методом краплинного лиття. Шар поруватого кремнію (PS) був виготовлений за допомогою фотоелектрохімічного травлення. Щільність прикладеного струму становить 20 мА/см^2 із зеленим лазерним випромінюванням, а типовий час фотоелектрохімічного травлення становив близько 15 хв. Коли зразки F-SWCNTs та F-MWCNTs піддавалися впливу газу NO_2 при різних робочих температурах, результати відгуку чутливості показують, що F-SWCNTs мають кращі показники, ніж F-MWCNTs. При 200 °C, чутливість F-SWCNTs/PS досягає 61 %, час відгуку та час відновлення становили відповідно 10 с і 214 с, тоді як для F-MWCNTs/PS чутливість сягає 57 % при 100 °C, час відгуку та час відновлення складали приблизно 20 с і 647 с відповідно. У той же час, F-MWCNTs мають робочу температуру (100 °C) меншу за температури F-SWCNTs (200 °C).

Ключові слова: F-SWCNT, F-MWCNT, Окислювальний газ, Чутливість, Час реакції, Поруватий кремній.