Sensitivity Performance of Single Wall Carbon Nanotubes Gas Sensor on Silicon and Porous Silicon

To cite this article: Asama N Naje and Waleed K Mahmood 2018 IOP Conf. Ser.: Mater. Sci. Eng. 454 012070
Sensitivity Performance of Single Wall Carbon Nanotubes Gas Sensor on Silicon and Porous Silicon

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Abstract. Pure single walled carbon nanotubes (pure-SWCNTs) and Functionalized single walled nanotubes (F-SSWCNTs) have been utilized to the manufactured nitrogen dioxide gas sensor. CNTs films have been deposited on (n-type) silicon and porous silicon substrate by drop casting method. A porous silicon layer (PS) was prepared via electrochemical etching. The applied current density was 20 mA/cm², and the typical electrochemical-etching time was chosen to be about 20 minutes. Upon exposure to fixed test gas mixing ratio (air: gas) NO₂ at different operating temperatures, the sensitivity response results show that Pure single walled carbon nanotubes and Functionalized single walled nanotubes deposited on porous silicon have better performances than that deposited on silicon. At RT the F-SWCNTs/Ps sensitivity reaches to 36%, the response and recovery time is about 11 s and 26 s, whereas for SWCNTs/Ps the sensitivity 13.5%, the response and recovery time is about 13 s and 24 s.

Keywords: F-SWCNTs; oxidizing gas; sensitivity; response time; silicon; porous silicon.

1. Introduction
Nanotechnology deals with developing materials, devices, or other structures having at least one dimension ranging from 1 to 100 nanometers. One of the early applications of nanotechnology is in the field of nanosensors. Nanosensors are any chemical or biological sensors used to convey information through nanomaterials [1]. A chemical nanosensor is an electronic device whose operation relies on at least one of the physical and chemical properties of the nanoscale [2]. The nanostructure-based nanosensor devices have a number of salient characteristics, including high sensitivity and excellent selectivity. These properties set them apart from currently available sensor technologies [3]. As a nanotube is a surface structure, its whole weight is concentrated in its surface layers, this feature is the origin of the uniquely large unit surface of tubules which in turn predetermines their electrochemical and adsorption properties [4]. The high sensitivity of the electronic properties of nanotubes to molecules adsorbed on their surface and the unparalleled unit
surface providing for this high sensitivity make CNT a promising starting material for the development of super-miniaturized chemical and biological sensors [5]. Porous silicon (PS) is a quite new material in the field of gas sensors, except for its well-known sensitivity to humidity; it is very interesting for its high surface to volume ratio and reactivity to the environment. Many features of this material have been used for gas detection, such as work function, refractive index, photoluminescence and conductivity variation [6], the latest being the easiest way to realize a gas sensor. The present work study the sensing performance of the SWCNTs and F-SWCNTs as NO\textsubscript{2} gas sensor deposited on silicon and porous silicon and make comparisons between them to get the best performance.

2. Experimental work

2.1 Preparation of the samples

In this work, 2x2cm\textsuperscript{2} dimensions primary n-type silicon wafer substrates were thoroughly cleaned to de-contaminate their surface from any available stains and dirt. A porous silicon layer (PS) was prepared via 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\textsuperscript{2}, and the typical electrochemical-etching time was chosen to be about 20 minutes. To prepare CNT sample, 0.02 g of the CNT was dispersed in Dimethylformamide (DMF). A magnetic stirrer was incorporated for this purpose for 15 minutes, followed by 1 hour sonication. The obtained solution was used for film deposition on porous silicon by the drop casting method. To prepare CNT sample, 0.01 g of CNT was dispersed in Dimethylformamide (DMF). A magnetic stirrer was incorporated for this purpose for 15 minutes, followed by 1 hour sonication. The obtained solution was used for film deposition on porous silicon by the drop casting method.

2.2. Gas sensor testing system

The detail of the gas sensor testing unit, which was used in the current tests, was described elsewhere [7]. A steel cylindrical test chamber of diameter 163 mm and of height 200 mm with the bottom base made removable and of O-ring sealed. The effective volume of the chamber was 4173.49 cc, which had an inlet for allowing the test gas to flow in and an air admittance valve allowing atmospheric air after evacuation. Another third port was provided for the vacuum gauge connection. A multi-pin feed through at the base of the chamber allowed for the electrical connections to be established to the sensor and the heater assembly. The heater assembly consisted of a hot plate and a k-type thermocouple inside the chamber in order to control and set the desired operating temperature of the sensor. The thermocouple sensed the temperature at the surface of the film exposed to the analyte gas. The PC-interfaced multi meter, of type UNI-T UT81B, was used to register the variation of the sensor conductance (reciprocal of resistance) exposed to predetermined air – NO\textsubscript{2} gas mixing ratio. The chamber can be evacuated by using a rotary pump to a rough vacuum of 2\times10\textsuperscript{-2} bar. A gas mixing manifold was incorporated to control the mixing ratios of the test and carrier gases prior to being injected into the test chamber. The mixing gas manifold was fed by zero air and test gas through a flow meter and needle valve arrangement. This arrangement of mixing scheme was done to ensure that the gas mixture entering the test chamber was premixed thereby giving the real sensitivity.

3. Results and discussion

In the figure (1), long nanotubes with large agglomerates and closely packed CNTs can be seen.
Figure 1. SEM images of SWCNTs film.

Figure (2) shows the EDX spectrum of SWCNTs. Thin films were deposited on n-type PS wafers. The EDX trace confirms qualitatively the existence of the carbon (C) and silicon (Si) elements, where the thickness of SWCNTs is 0.112 µm.

Figure 2. EDX spectrum of SWCNT thin film deposited on porous silicon substrate.

X-ray diffraction was used to study the crystal structure of SWCNTs powder. Figure (3) displays the XRD patterns for the CNTs powder for SWCNTs. The diffraction pattern SWCNTs appeared at 2θ of 26° and 44.5°. The 2θ peaks corresponds to (002) and (100) reflection planes or also known as interlayer spacing between adjacent graphite layers and these peaks reflect hexagonal structure. This is in agreement with results reported by other researchers [8].
Table (1) shows the grain size of SWCNTs from X-ray diffraction pattern and by using Scherer's formula Eq formula [8]:

$$D = \frac{0.99 \lambda}{\Delta(2\theta) \cos(\theta)}$$

...(1)

Table 1. Crystalline size of the CNTs powder as estimated via the Scherer formula.

| CNT type  | 2Theta (degree) | Cos θ | β (rad) | Crystalline size D (nm) | hk1 | Average crystalline size (nm) |
|-----------|-----------------|-------|---------|-------------------------|-----|-------------------------------|
| SWCNTs    | 26              | 0.974 | 0.122   | 1.16                    | 002 | 1.325                         |
|           | 44.5            | 0.925 | 0.104   | 1.49                    | 100 |                               |

The surface morphology and topography of the porous silicon layer observed from the AFM micrograph is shown in figure (4). It is observed that nanoporous silicon had a regular distribution and homogeneous porous and the average surface roughness was 6.93 nm, 31.96 nm high and average porous size was 77.47 nm.
Figure 4. AFM image of the porous silicon layer.

The atomic force microscopic (AFM) of the PSi/CNTs is shown in Fig. 5. Results of surface morphology of the CNTs film had a good uniform surface homogeneity and good indication for having nanoporous with a regular distribution of the CNTs. The average surface roughness was 3.42 nm, 13.48 nm high and average porous size 96.23 nm.

Figure 5. AFM images for the SWCNTs deposited on PS nanosurface.

The sensor response (S) is defined as the ratio of the change in resistance (Rg – Ra) upon exposure to target analyte to the resistance (Ra) of the sensor in air.

\[ S = \left| \frac{R_{g2\text{H}} - R_{g25}}{R_{g25}} \right| \times 100\% \]  

.....(2)
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 [9].

3.1 Sensing characteristics of SWCNTs and F-SWCNTs on Si:
Their working principle is that adsorption of electron donating (NO\(_2\)) on the CNT surface result in charge transfer between the CNT and gas molecules [10]. In figure (6a, b), 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 [11].

![Figure 6. Resistance-time variation of SWCNTs sensor time at RT, 100 °C and 200 °C testing temperature upon exposure to NO\(_2\) gas for a) Pure-SWCNTs and b) F-SWCNTs.](image1)

Figure 6. Resistance-time variation of SWCNTs sensor time at RT, 100 °C and 200 °C testing temperature upon exposure to NO\(_2\) gas for a) Pure-SWCNTs and b) F-SWCNTs.

Figure (7) shows the sensitivity S% of CNTs to NO\(_2\) gas. The test performed at 1:1, NO\(_2\): air gas mixing ratio. It is shown that the sensitivity increased with increasing the operating temperature T. The maximum sensitivity of pure-SWCNTs of 13% was obtained 200°C testing temperature after which it began to drop with increasing T. While the sensitivity of F-SWCNT of 16.9% was obtained at 200°C testing temperature after which it began to drop with increasing T.

![Figure 7. Sensitivity of CNTs thin film at various testing temperatures upon exposure to 1:1, NO\(_2\) gas: air for pure-SWCNTs and F-SWCNTs on Si substrate.](image2)

Figure 7. Sensitivity of CNTs thin film at various testing temperatures upon exposure to 1:1, NO\(_2\) gas: air for pure-SWCNTs and F-SWCNTs on Si substrate.

Table (2) shows the sensitivity, response and recovery time for Pure SWCNTs and F-SWCNTs deposited on silicon upon exposure to the NO\(_2\) gas.
Table 2. The sensitivity, Response and Recovery time of Pure-SWCNTs/Si and F-SWCNTs/Si thin film upon exposure to NO₂ gas at different temperatures.

| Type            | T (°C) | S%  | tₛ (s) | tᵣ (s) |
|-----------------|--------|-----|--------|--------|
| Pure SWCNTs/Si | RT     | 2.6 | 6      | 12     |
|                 | 100    | 10.9| 4      | 6      |
|                 | 200    | 13  | 6      | 8      |
| F-SWCNTs/Si    | RT     | 6.8 | 10     | 12     |
|                 | 100    | 15.5| 6      | 10     |
|                 | 200    | 16.9| 12     | 14     |

The response and recovery times of SWCNTs gas sensor was 6 s and 8 s at 200 °C, while The response and recovery times for F-SWCNTs was 12s and 14s at 200 °C.

3.2 Sensing characteristics of pure-SWCNTs and F-SWCNT on Porous Silicon:
In figure (8a and b) 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 NO₂. This behavior may be attributed to the charge transfer occurring from CNTs to NO₂ because of its highly oxidizing nature.

Figure 8a. Resistance-time variation of SWCNTs sensor time at RT, 100 oC and 200 °C testing temperature upon exposure to NO₂ gas for a) Pure-SWCNTs and b) F-SWCNTs on PS substrate .

Figure (9) shows the sensitivity S% of CNTs deposited on Porous Silicon to NO₂ gas. The test performed at 1:1, NO₂: air gas mixing ratio. It is shown that the sensitivity decreased with increasing the operating temperature T. The maximum sensitivity of pure-SWCNTs/PS of 13.5% was obtained 100°C testing temperature after which it began to drop with increasing T. While the sensitivity of
F-SWCNT/PS of 36% was obtained at RT °C testing temperature after which it began to drop with increasing T.

Figure 9. Sensitivity of CNTs thin film at various testing temperatures upon exposure to 1:1, NO2 gas: air for pure-SWCNTs and F-SWCNTs.

Table (3) shows the sensitivity, response and recovery time for Pure SWCNTs/PS and F-SWCNTs/PS upon exposure to the NO2 gas. The response time of the CNTs gas sensor decreases with increasing the operating temperature, with the shortest response and recovery times being at about 13s and 24s, respectively at 100°C for Pure-SWCNTs and 11s and 26s at RT for F-SWCNTs.

Table 3. The sensitivity, Response and Recovery time of Pure-SWCNTs/PS and FSWCNTs/PS thin film upon exposure to NO2 gas at different temperatures.

| Type            | T (°C) | S%  | t_s (s) | t_c (s) |
|-----------------|--------|-----|---------|---------|
| Pure SWCNTs/PS  | RT     | 16  | 16      | 27      |
|                 | 100    | 13.5| 13      | 24      |
|                 | 200    | 11.7| 8       | 20      |
| COOH-SWCNTs/PS  | RT     | 36  | 11      | 26      |
|                 | 100    | 29.7| 8       | 13      |
|                 | 200    | 23  | 14      | 18      |

By the comparison between tables (3.4) and (3.5) we can see that the maximum sensitivity of Pure-SWCNTS and F-SWCNTs was at operating temperature 200 °C, the sensitivity was for F-SWCNTs (S = 16.9%) higher than sensitivity of Pure-SWCNTs (S = 13%), for deposition of Pure-SWCNTs and F-SWCNTs on silicon. While for deposition of Pure-SWCNTs and F-SWCNTs on porous silicon the maximum sensitivity increased with decreasing temperatures at operating temperature 100 °C for Pure-SWCNTs and R.T. for F-SWCNTs (13.5% and 36%), respectively. This can be attributed to the functionalization of CNTs by adding the carboxyl group —COOH. Using
functionalized SWCNTs 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. And also attributed for deposits of CNTs on porous silicon because porous silicon have large surface-to-volume ratio, which in turn will cause to more dispersion of the CNTs and thus increasing the surface to volume ratio of interaction between CNTs and NO2 gas.

4. Conclusion

Comparative gas sensing property analysis of the SWCNT and F-SWCNTs nanocomposite based gas sensors on silicon and porous silicon revealed excellent sensor performance for F-SWCNTs/Ps nanocomposite based sensor compared to SWCNT/Ps for NO2 which is attributed to the presence of functionalization of CNTs by adding the carboxyl group (−COOH) to SWCNT. Moreover, fast response and good reversibility were observed for the F-SWCNTs/Ps based sensor compared to the SWCNTs 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 NO2 gas. The study explores the possibility of using F-SWCNTs/Ps based on, the low cost and low temperatures for the sensing of NO2 gas. The sensor device (F-SWCNTs/Ps) has proved highly efficient in use as a sensor to detect NO2 gas. And it could open prospects for development as a result that chemical sensor may reach the level of dealing with one molecule of gas and shorten the sensor response time. 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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