Enhancement of Functionalized Carbon Nanotubes Gas Sensor by Adding Metal Oxide Nanoparticles

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Abstract

Functionalized-multi wall carbon nanotubes (F-MWCNTs) and functionalized-single wall carbon nanotubes (F-SWCNTs) were well enhanced using Cobalt oxide (CoO) Nanoparticles. The sensor structure consists of a layer of material (F-MWCNTs/CoONPs) and (F-SWCNTs/CoO NPs) by adding 0.0005g of CoONPs to 1.5ml of the CNTs mixtures which are deposited on n-type porous silicon (PS) by the drop casting method. These two sensors have high sensitivity to NO₂ at room temperature. The analysis indicated that the (Functionalized-MWCNTs/CoONPs) have a better performance than (Functionalized-SWCNTs/CoONPs) when exposed to NO₂ gas. The F-SWCNTs/CoONPs gas sensor showed sensitivity about (19.1 %) at room temperature with a response time of 17 seconds, while F-MWCNTs/CoONPs sensor showed better sensitivity (39 %) at room temperature with a response time of 13 seconds. The sensor shows very repeatable sensor performance, complete recovery and adequate response.

Key words

F-SWCNTs, F-MWCNTS, metal oxide, NO₂ sensor.

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Introduction

Expanding worries about pollution have prompted a rising need for gas sensors for a wide scope of utilizations. Metal oxide gas sensors have been broadly utilized for the discovery of various gases [1].

Transitional metal oxide nanoparticles are an important class of inorganic nanomaterials that have been extensively investigated due to their fascinating catalytic, magnetic and electronic properties compared with their bulk equivalents and for their wide variety of potential applications compared with bulk material [2]. Among the transition metal groups, cobalt oxide is a well-recognized ferromagnetic semiconductor nanomaterial that has created a focus on sensors, magnetic materials, and electrochemical devices due to its possible applications. Co$_3$O$_4$ and CoO are amongst various types of cobalt oxides because of their distinctive structural environments and properties [3].

Recently, CNTs has pulled in an extraordinary interest owing to its unique electrical, chemical and mechanical properties. This makes the carbon nanotubes a promising material for a variety of potential applications [4]. Previous work have shown that carbon nanotubes can distinguish a wide range of gases at close room temperature, such as NO$_2$ and NH$_3$, so it is a perfect contender as a detecting material [5, 6].

As a chemical sensor, gas-detecting at low temperatures is of uncommon intrigue in view of low-vitality utilization. In order to increase its sensitivity, many methods have been described to increase the sensitivity of gas chemical resistors that rely on carbon nanotubes (CNT) functionalized with noble metal Au, Ag and Pt nanoclusters. Zhang et al. have grown a highly sensitive NO$_2$ sensor which appears to rely on undecorated SWCNTs monolayer junctions [7].

The use of carbon nanotubes decorated with metal nanoparticles has been proposed with promising results to improve the chemical selectivity of gas sensors [8].

In the present work functionalized carbon nanotubes (SWCNTs and MWCNTs) were decorated with metal oxide (CoO) nanoparticles to prepare NO$_2$ gas sensor. Comparisons between the two devices' behavior before and after adding CoONPs was made and finally the sensor parameters were studied.

Experimental work

1. Preparation of porous silicon

The N-type silicon wafer layer (1×1 cm$^2$) with <0.02Ω resistivity was used in this work. The porous silicon layer (PS) was prepared using photo-etching technique. The following steps were taken:

The silicon wafers were thoroughly cleaned and purified using distilled water and ethanol. The wafers were immersed in 40% HF acid, blended with ethanol of the ratio (1:1) all put in a Teflon beaker. The samples were irradiated with green laser radiation with an applied current density of 20mA/cm$^2$. The photo-electrochemical etching process was held for 15 min.

2.2 Preparation of carbon nanotubes samples

The carbon nanotubes used for this work were functionalized single-walled and multi-walled carbon nanotubes. F-SWCNTs were of (1-2nm OD, ~30μm length, 2.73wt% COOH content, >90wt% purity) and F-MWCNTs were of (20-30nm OD, ~30μm length, 1.23wt% COOH content, >95wt% purity).
To prepare carbon nanotubes, 0.005g of both F-SWCNTs and F-MWCNTs were dispersed in 20ml Dimethylformamide (DMF) in separate tubes. The solution was magnetically stirred for 4hr followed by 2hr sonication.

3. Enhancement of carbon nanotubes using Cobalt oxide nanoparticles
CoO nanoparticles (diameter <100nm) were supplied by Sky Spring Nanomaterials, Inc. 0.0005g of CoONPs was dissolved in 1.5ml of the CNTs mixtures. The solutions were put in a glass flask and were stirred for 4 hours using a magnetic bar, followed by a 2hr sonication. Using the drop-casting process, the mixture was deposited on porous silicon and left to dry at room temperature. The sample is then prepared for the gas sensing experiment.

Results and discussion
1. Structural interpretations
Structural characteristics of CoO nanoparticles were obtained using X-ray diffractometer (XRD). The X-ray diffraction pattern displayed diffraction peaks absorbed at 2θ values (Fig. 1). The average crystallite size (D) of CoO nanoparticles was calculated by the Scherer equation [9] which is:

\[ D = \frac{k \lambda}{\beta \cos \theta} \]  

where K is the constant of proportionality and \( \lambda \) is the x-ray wavelength used (\( \lambda = 1.542 \, \text{Å} \)), \( \beta \) is the full width at half maximum (FWHM) of the line, and \( \theta \) is the diffraction angle.

As for CoO, the Bragg’s angle (20) at 31.48º, 37.11º, 59.62º, 65.43º had the reflection planes (220), (311), (400), (511), (440) respectively [10], which agrees with the standard data (JCPDS card file no. 76-1802). This shows that we have a polycrystalline structure with the Face-centered cubic phase (F.C.C.) structure. The crystalline size D for the produced powder nanoparticles was calculated according to the Scherer Equation. The average diameter of CoO NPs was found to be (20nm).

3. Morphological analysis
Fig.2 displays SEM images for the impregnated F- SWCNTs of metal oxides. The tubular geometry of the F-SWCNTs was observed and after impregnation no damage was noticed in the CNTs structures. In general, after impregnation with
metal oxide nanoparticles the dispersion of F-SWCNTs had improved. Nanoparticles of metal oxide can help to reduce the strong van der Waals forces between CNTs, contributing to their improved dispersion.

Fig.2: SEM image of F-SWCNT/CoO nanoparticles.

3. Chemical gas sensing measurements
3.1 Sensing measurements of F-SWCNTs on PS

The sensor response (S) is defined as the ratio of the change in resistance (Rg – Ra) to the sensor’s resistance (Ra) in air when exposed to the analytic target, the equation below is specified for oxidizing gases [11].

\[
s = \left( \frac{R_{\text{gas}} - R_{\text{air}}}{R_{\text{air}}} \right) \times 100\%
\]  

(2)

where, Rg is resistance in the presence of gases and Ra the resistances in air. The response time and recovery time were measured as the time taken by the sensor from its initial resistance to attain 90 percent of the total resistance change (t₉₀).

The working theory of the sensor is the adsorption of electron donation (NO₂) on the CNT side, resulting in the transfer of charge between the CNT and the gas molecules. Figs.3 (a, b, c, and d) show the resistance as a function of time. Experimental results showed increased CNTs conductance when exposed to oxidizing gases such as NO₂. Because of its highly oxidizing nature. This behavior may be attributed to the charge transfer occurring from CNTs to NO₂ because of its highly oxidizing nature. When oxidizing gases like NO₂ are adsorbed on the surface of p-type CNTs, the Fermi levels are shifted towards the valence band, generating more holes and thus enhancing conductivity.
F-SWCNTs sensing parameters are shown in Table 1. At RT, which is considered the optimum temperature, the maximum sensitivity value (23%) was reached. The response and recovery times were 4 s and 33 s respectively at RT. The activation energy can suffice at the optimum temperature to complete the chemical reaction. The rise and decrease in sensitivity means that the gas is adsorbed and desorbed. It can also be noticed from the table that the response time of the F-SWCNTs sensor changes as the temperature rises.

Fig.3: Resistance-time variation of F-SWCNTs sensor time at a-RT, b-50 C°, c-100 C°, d-150 C° and e-200°C testing temperature upon exposure to NO₂ gas.
Table 1: The sensitivity (S), Response (tₚ) and Recovery time (tₑ) of F-SWCNTs/Porous Silicon thin film when exposed to NO₂ gas at different temperature.

| Type         | T(°C) | S%  | tₚ (s) | tₑ (s) |
|--------------|-------|-----|--------|--------|
| F-SWCNTs/PS  | RT    | 23  | 4      | 33     |
|              | 50    | 1.06| 6      | 142    |
|              | 100   | 7.1 | 22     | 653    |
|              | 150   | 3.07| 12     | 346    |
|              | 200   | 5.8 | 10     | 214    |

3.2 Sensing measurements of F-MWCNTs on PS
The variation of resistance with time is shown in Fig.4 (a, b, c, and d). Experimental results revealed an increase in F-MWCNT conductivity when exposed to oxidizing gases such as NO₂. This activity can be due to the charge transfer occurring from CNTs to NO₂ because of the highly oxidizing nature of NO₂.

Fig.4: Resistance-time variation of F-MWCNTs sensor time at a-RT, b-50 °C, c-100 °C, d-150 °C and e-200 °C testing temperature upon exposure to NO₂ gas.
F-MWCNTs gas sensor parameters when exposed to NO$_2$ gas are shown in Table 2. The response time varies with the rise of operating temperature. The maximum sensitivity was (57 %) at 100 °C, with the response and recovery times at approximately 17s and 647s respectively.

Table 2: The sensitivity($S$), Response ($t_r$) and Recovery time ($t_c$) of F-MWCNTs/porous silicon film when exposed to NO$_2$ gas with different temperatures.

| Type          | T(°C) | S% | $t_r$(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      |

By comparing Table 1 with 2 it can be seen that the maximum sensitivity of F-SWCNTs is 23% at room temperature (RT) and while the maximum sensitivity of F-MWCNTs is 57% at operating temperature 100 °C, Maximum sensitivity of F-SWCNTs is obtained at a lower operating temperature than that of F-MWCNTs, which makes it the best as a sensor.

The sensor reaction of F-SWCNTs films is lower at any operating temperature than that of thin film F-MWCNTs. The outcomes show that the Functionalized-multi walled carbon nanotubes perform preferably than single walled carbon nanotubes, and these outcomes rely unequivocally upon the structure of CNTs. The charge carriers of F-SWCNTs are electrons that is the reason for the increase in resistance when exposed to NO$_2$ gas but in F-MWCNTs the charge carriers are holes which leads to a decrease in resistance when exposed to NO$_2$ gas.

When the configuration of atoms in a CNTs limits the collisions between atoms and electrons of the conduction, a CNTs is profoundly conductive. The strong carbon atom bonds also allow CNTs to withstand higher electrical currents than other material. And if the diameter of the tubes decreases the current rises [12].

3.3 Sensing performance of Functionalized- Single walled CNTs/CoO NPs and Functionalized-Multi walled CNTs/CoO NPs

The change of resistance as a function of time is shown in Figs. 5 and 6. Experimental results revealed an improvement in F-MWCNTs / CoO NPs and F-SWCNTs / CoONPs conductivity when exposed to oxidizing gases such as NO$_2$.

In view of its exceptionally oxidizing nature, this activity can be attributed to the charge transfer occurring from CNTs to NO$_2$. 


Fig. 5: Resistance-Time curve of F-MWCNTs/CoO NPs sensor at RT, 50 °C, 100 °C, 150 °C when exposed to NO₂ gas.
Fig. 6: Resistance-Time curves of FSWCNTs/CoO NPs sensor at RT, 50 °C, 100 °C, 150 °C when exposed to NO$_2$ gas.

From Table 3, it can be seen that the sensitivity of the F-MWCNT/CoO NPs device is much higher than that of the F-SWCNT/CoO NPs/PS. The sensitivity is shown to decrease with rising operating temperature $T$. At room temperature, the maximum sensitivity of FSWCNTs / CoO NPs was 19.1 % and for F-MWCNTs /CoO NPs was 39%, after that it started to fall with the rise in temperature.

Table 3: The sensitivity (S), response time, and recovery time of F-MWCNTs/CoO NPs and F-SWCNTs/CoO NPs when exposed to NO$_2$ gas.

| Type               | Temp.      | S%   | Response time | Recovery time |
|--------------------|------------|------|---------------|---------------|
|                    | R.T.       | 39%  | 13s           | 280s          |
| F-MWCNTs/CoONPs   | 50°C       | 28%  | 19s           | 176s          |
|                    | 100°C      | 18%  | 16s           | 100s          |
|                    | 150°C      | 13%  | 14s           | 70s           |
|                    | R.T.       | 19.1%| 17s           | 222s          |
| F-SWCNTs/CoONPs   | 50°C       | 15.5%| 25s           | 130s          |
|                    | 100°C      | 12.1%| 26s           | 65s           |
|                    | 150°C      | 10.2%| 19s           | 55s           |

At room temperature, which is called optimum temperature, the maximum sensitivity value was obtained. The activation energy can suffice at the optimum
temperature to complete the chemical reaction. The rise and decrease in sensitivity show the gas adsorption and desorption phenomenon.

Using functionalized CNTs, strong acids that leave holes functionalized with oxygenated functional groups (-COOH) can provide open side walls because of oxidative damage to the nanotube structure. Treatment of CNTs with strong acids will in general open these channels, which expands the gas adsorption in the wall of the carbon nanotubes and so sensitivity increases. Furthermore since carbon nanotubes are deposited on porous silicon (PS) which has a high surface-to-volume ratio, more carbon nanotubes dispersion will be induced thus increasing the interaction between carbon nanotubes and NO$_2$ gas [13].

**Conclusions**

By comparing gas detection conduct behavior between the F-MWCNTs and F-SWNCTs before and after adding cobalt oxide nanoparticles, the F-MWCNTs/CoONPs was found to achieve adequate room temperature gas sensor performance compared to F-SWCNTs/CoONPs for NO$_2$ gas, which is associated with the presence of cobalt oxide nanoparticles and the functionalization of carbon nanotubes. The F-MWCNTs/CoONPs Nano composite was observed to be sensitive to NO$_2$ gas at room temperature (S=39%). This research seeks the opportunity of utilizing F-MWCNTs/CoONPs because of its high sensitivity in low temperatures as well as its enhanced surface activity. The sensor device (F-MWCNTs/CoONPs) has exhibited profoundly dynamic behavior being used as a sensor to recognize NO$_2$ gas. The sensor device in the present work approves a high efficiency and sensitivity, a short response and recovery time, low operating temperature and stability in its behavior.

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