Parametric Analysis of NO$_2$ Gas Sensor Based on Carbon Nanotubes

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Abstract: Two types of carbon nanotubes [single walled nanotubes (SWCNTs) and multi walled carbon nanotubes (MWCNTs)] are deposited on porous silicon by the drop casting technique. Upon exposure to test gas mixing ratio 3% NO$_2$, the sensitivity response results show that the SWCNTs' sensitivity reaches to 79.8%, where MWCNTs' is 59.6%. The study shows that sensitivity response of the films increases with an increase in the operating temperature up to 200°C and 150°C for MWCNTs and SWCNTs. The response and recovery time is about 19 s and 54 s at 200°C for MWCNTs, respectively, and 20 s and 56 s at 150°C for SWCNTs.

Keywords: SWCNTs; MWCNTs; NO$_2$ gas; sensitivity; response time

1. Introduction

Detecting gas molecules is basic to environmental monitoring, control of chemical processes, space mission, agricultural and medical applications. The sensing of NO$_2$ is important to monitor environmental pollution resulting from combustion or automotive emissions [1]. Nitrogen dioxide (NO$_2$) is flammable, colorless, and dangerous, even at very low concentration. Moreover, the interaction of NO$_2$ and CO in sunlight tends to produce O$_3$, which is believed to be harmful to plants and the respiratory system of human beings and animals because of its strongly oxidizing behavior. Therefore, from the public health and environmental protection viewpoint, the sensitive detection of nitrogen dioxide is of great scientific importance [2].

A gas sensor is a device which detects the presence of different gases in a region, particularly those gases which might be harmful to humans or animals. The development of the gas sensor technology has received considerable attention in recent years for monitoring environmental pollution. It is well known that chemical gas sensor performance features, such as sensitivity, selectivity, time response, stability, durability, reproducibility, and reversibility, are largely influenced by the properties of the sensing materials used [3] .The basic principle behind gas detection is a change in an electrical property of the detecting material upon exposure to the gas. For example, in the case of carbon nanotubes, the resistance changes with exposure to different gases like NO$_2$ and NH$_3$. Other electrical properties of nanotubes like thermoelectric power and dielectric properties also change upon gas exposure [4]. Common gas sensors are metal oxide semiconductor such as tin oxide, zinc oxide, titanium oxide, and aluminum oxide. Problems encountered with these sensors are lack of flexibility

and poor response time, and it is operated at the elevated temperature [5]. But nowadays, researchers' goal is to develop the sensors, which can operate at room temperature and consume low power. Carbon nanotubes (CNTs) based sensors have been recently studied due to their excellent electrical, mechanical, and sensing properties. Because of the high surface area, CNTs can adsorb large amount of gases, which make them a probable contender for a gas sensor with very high sensitivity and low response time. Particularly, gas adsorption in CNTs is an important issue for both fundamental research and technical applications [6]. There are two types of carbon nanotubes' morphology. Single-walled nanotubes (SWNTs) consist of a honeycomb network of carbon atoms and can be visualized as a cylinder rolled from a graphitic sheet. The other is multi-walled nanotubes (MWNTs) that are a coaxial assembly of graphitic cylinders generally separated by the plane space of graphite [7].

The present study focuses on the synthesis and chemi-resistive characteristics of carbon nanotubes (CNTs) thin film sensor. The material is prepared by a simple chemical solution method and the thin films are fabricated by drop-coating method.

2. Experiment

2.1 Preparation of the samples

In this work, $2 \times 2 \, cm^2$ 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 photochemical wet etching. This process was carried out by using ordinary light source. Its main apparatus consisted of a Quartz Tungsten Halogen lamp (250 W), a focusing lens (3.8 cm) with focal length, and the diluted etching HF acid of 50% concentration mixed with ethanol in (1:1) ratio in a Teflon container. 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 [8]. 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_2 gas mixing ratio. The chamber can be evacuated by using a rotary pump to a rough vacuum of 2×10^{-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

The response of a sensor upon the introduction of a particular gas species is called the sensitivity (S).

The most general definition of sensitivity applied to solid state chemi-resistive gas sensors is a change in the electrical resistance (or conductance) relative to the initial state upon exposure to a reducing or oxidizing gas component. It is calculated by using the equations below [9]:

$$S = \frac{\Delta R}{R_o} \times 100\% = \left| \frac{R_{gas} - R_{air}}{R_{air}} \right| \times 100\% \qquad (1)$$

or

$$S = \frac{\Delta G}{G_o} \times 100\% = \left| \frac{G_{gas} - G_{air}}{G_{air}} \right| \times 100\% \qquad (2)$$

where R is the electrical resistance, G is the electrical conductance, and the subscript "air" indicates that background is the initial dry air state and the subscript "gas" indicates the analyte gas has been introduced.

Figure 1 shows the scanning electron microscope (SEM) images for the MWCNT and SWCNTs deposited on PS. In these figures, long nanotubes with large agglomerates and closely packed CNTs are shown.
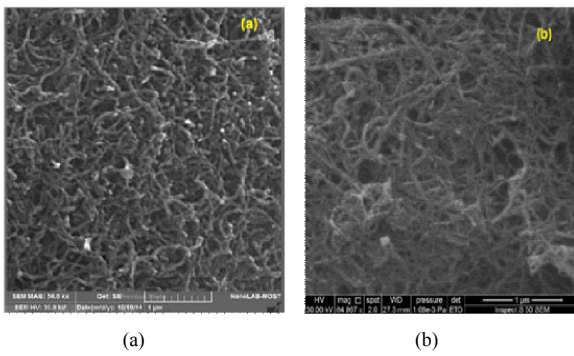

(a) (b)

Fig. 1 SEM images for the CNT on PS: (a) MWCNTs and (b) SWCNTs.

The atomic force microscopic (AFM) of the PSi/CNTs is shown in Fig. 2. Results of surface morphology of the CNTs film had a good uniform surface homegensity and good indication for having nanoporous with a regular distribution of the CNTs. The roughness average (Sa) for this layer of PSi/CNTs was 1.04 nm while the root mean square roughness (Sq) was 1.24 nm and ten point height (Sz) was 5.86 nm.
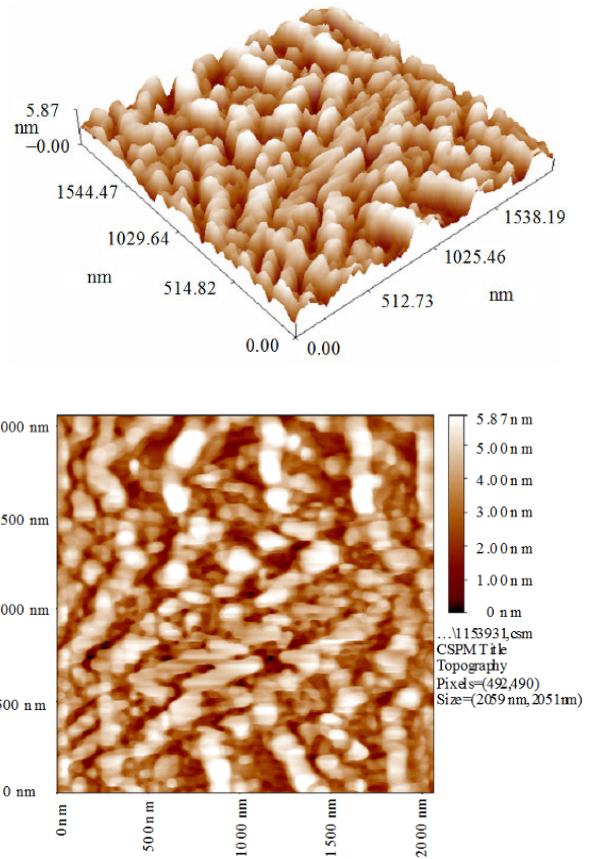

Fig. 2 AFM images for the CNTs deposited on PS.

Figure 3 shows the response of the MWCNTs and SWCNTs thin films upon exposure to NO₂ gas for mixing ratio 3% and at varying operating temperatures. It can be seen that the response of the films increases as the operating temperature increases up to 200℃ and 150℃, for MWCNTs and SWCNTs, respectively, and then decreases. The gas-sensing response increases with temperature in the 50℃ – 200℃ and 50℃ – 150 ℃ ranges for MWCNTs and SWCNTs, respectively, because thermal energy helps the reactions involved overcome their respective activation energy barriers. However, if the operating temperature becomes too high (i.e., >150 ℃ for SWCNTs or 200℃ for MWCNTs), the adsorbed oxygen species at the sensing sites on the film surface will be diminished and less available to react with NO₂ molecules, thereby limiting the film's response.

As shown in Fig. 4, the sensitivity $S\%$ increases with increasing the operating temperature T, where

the maximum sensitivity of MWCNTs is 59.61%, at 200℃ of the testing temperature after which it begins to drop with increasing T and the test is terminated.

While the sensitivity of SWCNTs is 79.81% at 150℃ of testing temperature after which it begins to drop with increasing T and the test is terminated.
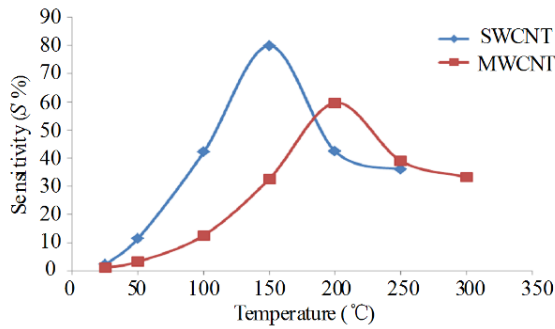

Fig. 3 Sensitivity variation with the operating temperature of the MWCNT and SWCNT gas sensor at 5 V bias voltage.
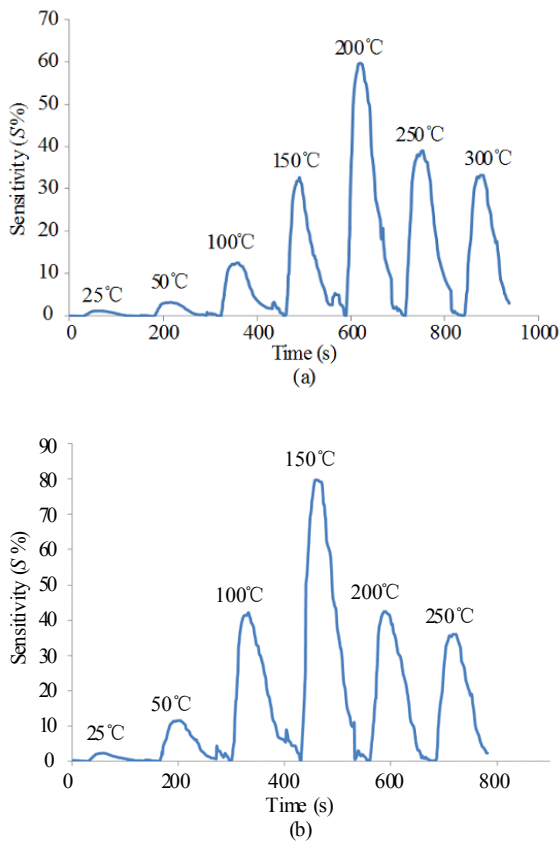

Fig. 4 Transient response of CNTs thin film at various testing temperatures upon exposure to NO₂ gas, 3% maxing ratio, at 5 V bias voltages for (a) MWCNTs and (b) SWCNTs.

At any operating temperature, the sensor response of the SWCNTs thin film is higher than

that of the MWCNTs thin film. The results show that SWCNTs have a better performance than MWCNTs, and these results strongly depend on the structure of CNTs. When the structure of atoms in a carbon nanotube minimizes the collisions between conduction electrons and atoms, a carbon nanotube is highly conductive. The strong bonds between carbon atoms also allow carbon nanotubes to withstand higher electric currents than material. So when the diameter of tubs decreases the current increases. Since SWCNTs have small diameter (1 nm–2 nm), it will have the higher conductivity and better performances [10].
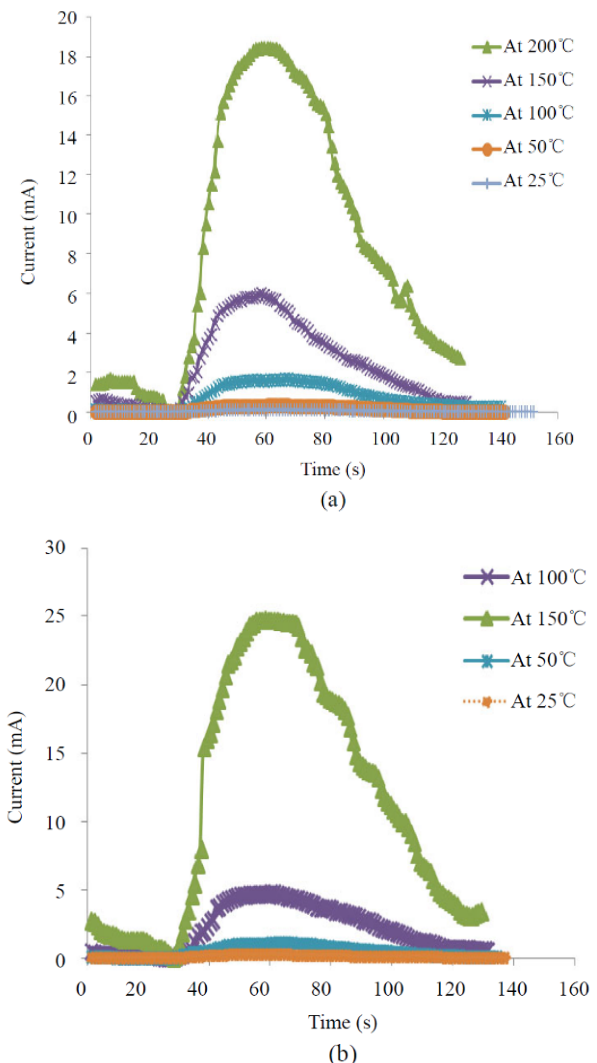

Fig. 5 Current-time variation of CNTs sensor time at 25℃, 50℃, 100℃, 150℃ and 200℃ testing temperature upon exposure to NO₂ gas and 5 V bias voltage for (a) MWCNTs and (b) SWCNTs.

The observed current appears in Fig. 5 increases (i.e resistance decreases) when exposing the CNT networks to NO_2, which can be due to that the electron transfer occurs from CNTs to NO_2 which has highly oxidizing natures. The variation of device resistance (or current) in the presence of oxidizing gas can be explained as follows: when oxidizing species like NO_2 are adsorbed on the surface of p-type CNTs, the Fermi levels are shifted towards valance band, generating more holes and thus decreasing the electrical resistance.

The response time of the CNTs gas sensor decreases with increasing the operating temperature, and with the shortest response and recovery time being at about 19 s and 54 s at 200 ℃ for MWCNTs, respectively, and 20 s and 56 s at 150 ℃ for SWCNTs.

In order to explain the results, the chemical nature of the NO_2 molecule is considered. Recent experimental results show that the electrical conductance of an individual semiconducting carbon nanotube strongly increases upon NO_2 gas exposure and the NO_2 is identified as an electron acceptor. In light of the present work, it is reasonable to propose that this behavior in the nanotube film is also due to adsorbed NO_2 in the tube wall. According to recent theoretical calculations, a possible interpretation of the electrical response of CNT films to NO_2 gas could be explained in terms of the physical absorption of this molecule. NO_2 has an unpaired electron and is known as a strong oxidizer. Upon NO_2 adsorption, a charge transfer is likely to occur from the CNTs to the NO_2 due to the electron-acceptor character of NO_2 molecules. The electrical response of the CNTs indicates that there is a charge transfer between the test gas and sensing element, and hence, the physisorption of gases in the nanotubes is the dominant sensing mechanism.

4. Conclusions

Thin films of two types of carbon nanotubes (SWCNTs and MWCNTs) were prepared by the drop casting method. The maximum variation of resistances to NO_2 was found at an operating temperature of around 200 ℃ and 150 ℃ for MWCNTs and SWCNTs. The response time was 19 s and 20 s for MWCNTs and SWCNTs, respectively.

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