

## Synthesis and Characterization of Carbon Nanotubes Hydrogen Gas Sensor

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### Abstract

Two types of carbon nanotubes (MWCNTs and SWCNTs) films were used to fabricate hydrogen gas sensors. CNTs films were deposited on porous silicon substrate by the drop casting method. The two sensors showed high sensitivity to hydrogen gas at different concentrations. Experimental results indicated that the SWCNTs have a better performance than MWCNTs. The SWCNTs gas sensor shows high sensitivity at 150°C with 29sec response time, whereas MWCNTs gas sensor shows best sensitivity at 200°C with 24sec response time.

**Keywords:** Hydrogen sensor, SWCNT, MWCNT, Sensitivity, response time.

### تصنيع وخصائص انابيب الكربون النانومترية كمتحسس لغاز الهيدروجين

#### الخلاصة

تم استخدام نوعين من انابيب الكربون النانومترية ( كاربون النانومترية ذو الجدار الواحد وانابيب الكاربون النانومترية المتعدد الجدران) كاقلام لتصنيع متحسس لغاز الهيدروجين. تم ترسيب انابيب الكاربون على السيلكون المنمش بطريقة التقطير. أظهر كلا المتحسسين تحسيسة جيدة لغاز الهيدروجين عند تراكيز مختلفة. بينت النتائج العملية ان لأنابيب الكاربون ذو الجدار الواحد اداء افضل من انابيب الكاربون المتعدد الجدران. أظهرت انابيب الكاربون النانومترية ذو الجدار الواحد تحسيسه عاليه عند درجه حراره 150 درجة مئوية مع زمن استجابته 29 ثانية بينما اكانت افضل نتائج التحسيسه لانابيب الكاربون المتعدد الجدران عند 200 درجة مئوية وبزمن استجابته 24 ثانية.

**الكلمات المفتاحية:** متحسس غاز الهيدروجين، كاربون النانومترية ذو الجدار الواحد، انابيب الكاربون النانومترية المتعدد الجدران، التحسيسه، زمن الاستجابة

### INTRODUCTION

Hydrogen is regarded as one of the best clean energy carriers, which is the ultimate fossil fuel candidate, with a high heat of combustion (142 kJ/g), low minimum ignition energy (0.017 mJ) and wide flammable range (4–75%), as well as high burning velocity [1]. Hydrogen (H<sub>2</sub>) is becoming the fuel for the next generation of automobiles. H<sub>2</sub> gas is highly explosive and flammable; therefore, the detection of the existence of a small amount in houses, vehicles, or industrial places is potentially important [2].

Sensors find applications in various fields of scientific and engineering disciplines ranging from controlling and monitoring chemical, machining process to biomedical devices. [3]. Gas sensors used in many factories and hospitals are important to environmental monitoring. In order to prevent the gas from leaking and angering the human body, it is necessary to detect chemical molecules and examine different gases [4]. In gas sensors, the active element that is sensitive to the target gas molecules is the key part and thus receives intensive attention. For example, after realizing the resistance of some semiconductor materials can be dramatically changed by the presence of gas molecules, many works have been directed to investigate them in gas sensors [5]. Since the report on the use of carbon nanotubes (CNTs) as a gas sensor, they have been investigated as materials of chemical sensor because they can detect small concentrations of molecules with a high sensitivity under ambient conditions (the large surface area of CNT provides a very large gas absorptive capacity) and the CNT sensor has a fast response. [6]. Carbon nanotubes are rolled-up graphene sheets occurring as single-wall (SWCNT) or multi-wall (MWCNT) cylinders. They have diameters from 0.4 up to a few nm, and their lengths range from a few nanometers up to several millimeters. [7].

The present work focuses on the sensing performance of CNTs Hydrogen gas sensors by using two types of the carbon nanotubes (MWCNT and SWCNT) and makes comparisons between them to get the best CNTs type and best performance.

## **Experimental Work**

### **Preparation of the samples**

In this work, (2x2 cm<sup>2</sup>) dimensions primary n-type silicon wafer substrates were thoroughly cleaned to de-contaminate their surface from any available stains and dirt. Porous silicon layer (PS) was prepared via photochemical wet etching. This process is carried out by using ordinary light source. Its main apparatus consists of a Quartz Tungsten Halogen lamp (250W) integrated with dichroic ellipsoidal mirror, a focusing lens, and the diluted etching HF acid poured 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 films deposition on porous silicon by the drop casting method.

### **Gas sensor testing system**

The details of the gas sensor testing unit which was used in the current tests is described elsewhere [8]. It is a steel cylindrical test chamber of 163 mm diameter and 200 mm height with the bottom base made removable and sealed by an O – ring sealed. The effective volume of the chamber is 4173.49 cc; it has an inlet for allowing the test gas to flow in and an air admittance valve to allow atmospheric air after evacuation. Another third port is provided for vacuum gauge connection. A multi-pin feed through at the base of the chamber allows for the electrical connections to be established to the sensor and the heater assembly. The heater assembly consists 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 senses 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 – hydrogen gas mixing ratio. The chamber can be evacuated using a rotary pump to a rough vacuum

of  $2 \times 10^{-2}$  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 is fed by zero air and test gas through a flow meter and needle valve arrangement. This arrangement of mixing scheme is done to ensure that the gas mixture entering the test chamber is premixed thereby giving the real sensitivity.

**Result and discussion**

Hydrogen absorption into carbon nanotubes samples at room temperature had no significant change in the resistance of carbon nanotubes. This is in a mutual agreement with results reported by other researchers [9, 10]. The carbon nanotubes need to be doped with other atoms or operated at higher temperature for them to be a good gas sensor for hydrogen. Sensitivity (S) 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 using the equation:

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

Or

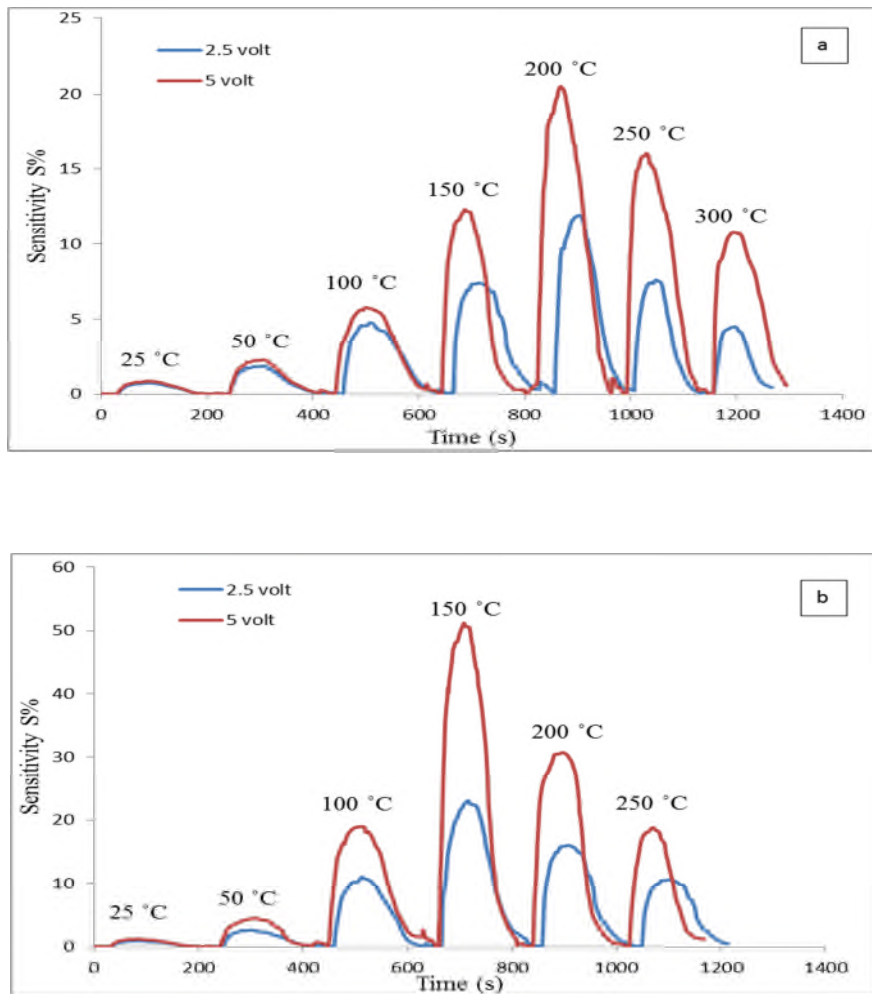
$$S = \frac{\Delta G}{G_o} \times 100\% = \left| \frac{G_{gas} - G_{air}}{G_{air}} \right| \times 100\% \quad \dots (2)$$

Where

R is the electrical resistance and 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.

Fig.1 shows the representative real – time electrical response of a thin film CNT sensing element to H<sub>2</sub> gas concentration of 3% in air. The test was performed at various sensing temperatures with 2.5 v and 5 v bias voltage.

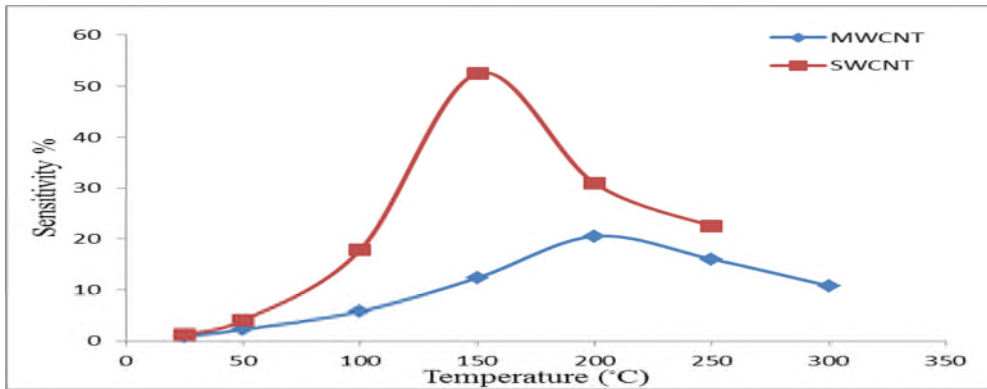
The sensitivity S% increased with increasing operating temperature T, where the maximum sensitivity of MWCNT is 11.93% and 20.50 % were obtained at 2.5 and 5 volt respectively at 200°C testing temperature after which it began to drop with increasing T and the test was terminated. the sensitivity of SWCNT is 21.84 % and 52.53 % were obtained at 2.5 and 5 volt respectively at 150°C testing temperature after which it began to drop with increasing T and the test was terminated.



**Figure (1) Transient response of CNT thin film at various testing temperatures upon exposure to 3 % H<sub>2</sub>: air gas mixing ratio and 2.5 and 5 bias voltages a) for MWCNT and b) for SWCNT.**

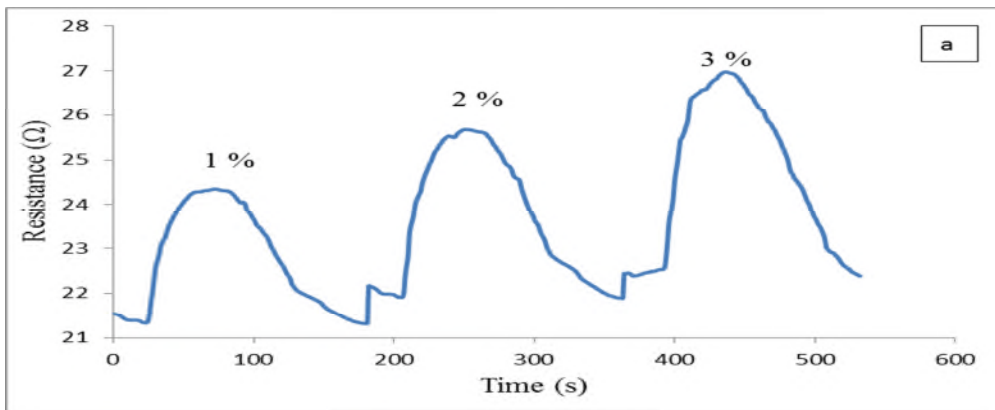
The sensitivity of the gas sensor at 5 volt bias voltage was found relatively higher than that of 2.5 volt. This dependence of sensing response on the operating temperature of the MWCNT film is exhibited in Fig.2. It is seen that the film maximum resistance goes through a maximum on changing T, with the best operating temperature at around 200 °C. Roughly speaking, the

increase of  $R_{max}$  (the left side of the maximum) results from an increase in the rate of surface reaction of the target gas, while the decrease of  $R_{max}$  (the right side) results from a decrease in the utility of the gas sensing layer. At the temperature of the maximum conductance (response), the target gas molecules have optimum penetration depth into the gas sensing grains (large utility) i.e., optimum reactivity for the diffusion in the whole sensing layer, as well as for exerting sufficiently large interaction with the surface (large gas response coefficient).



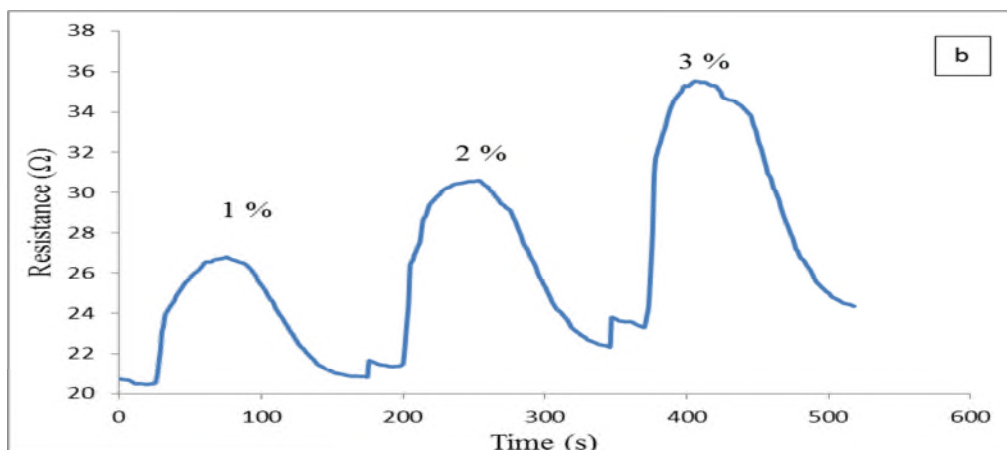
**Figure (2) Sensitivity variation with the operating temperature of the MWCNT and SWCNT gas sensor at 5 bias voltage and 3 % H<sub>2</sub>: air gas mixing ratio**

Fig.3 shows the sensitivity S variation with hydrogen gas concentration. Figure (1.a) shows the sensitivity S% increased with increasing hydrogen gas concentration for MWCNT, where the sensitivity of 14.27 %, 17.28 % and 20.50% was obtained in 1%, 2 % and 3% hydrogen: air gas mixing ratio respectively after which the current tends to saturate with increasing the analyte gas. A relatively short response time of about 24ses and recovery time of about 79ses was noticed at 3% hydrogen gas concentration.



**Figure (3-a) Transient response of MWCNTs gas sensor to different H<sub>2</sub>: air mixing ratios. The test performed at 200 degrees temperature and 5 v bias voltage**

Fig.3-b shows the sensitivity S% increased with increasing hydrogen gas concentration for SWCNT, where the sensitivity of 31.07 %, 43.27 % and 52.53% was obtained in 1%, 2 % and 3% hydrogen: air gas mixing ratio respectively after which the current tends to saturate with increasing the analyte gas. A relatively short response time of about 29 sec and a recovery time of about 89 sec were noticed at 3% hydrogen gas concentration.



**Figure (3-b) Transient response of SWCNTs gas sensor to different H<sub>2</sub>: air mixing ratios. The test performed at 150 degrees temperature and 5 v bias voltage**

The result of gas sensing data shows that H<sub>2</sub> molecule is a reduced agent that donates an electron to another species. Therefore, H<sub>2</sub> can play a role as an electron-donor and/or hole-acceptor. When the CNT gas sensor was exposed to H<sub>2</sub>, electrons were transferred from H<sub>2</sub> molecules to the CNTs. H<sub>2</sub> then donated its electrons to the valence band of the CNTs, thereby decreasing the number of holes by recombination, reducing the conductivity of CNTs, and increasing electrical resistance. Therefore, it is reasonable to assume that CNTs are a p-type semiconductor.

The sensitivity of the sensor increased as the concentration of H<sub>2</sub> increased. CNTs have four possible sites to which gas molecules can be adsorbed: internally, in interstitial channels, in external grooves, and on external surfaces. At a low concentration, the adsorption sites were not entirely filled by H<sub>2</sub> molecules. However, once the concentration of H<sub>2</sub> reached a critical level of 30%, the adsorption sites became completely filled, leading to saturation. When the concentration exceeded 30%, the adsorbed H<sub>2</sub> molecules became tightly packed on the CNT surfaces, the resulting is no more interactions between H<sub>2</sub> and CNTs.

### Conclusions

The best performance of CNTs (MWCNTs and SWCNTs) sensors used as hydrogen sensing were realized in the study. SWCNTs film provides good sensitivity to hydrogen gases more than MWCNTs (52.53% and 20.5%) respectively. The sensor temperature (150C° for SWCNT and 200C° for MWCNT) reduces the response to hydrogen gases from (29-24 Sec).

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