

## Research Article

## Enhanced Hydrogen Sensing Parameters of MWCNT – SnO<sub>2</sub> Thin Film

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### Abstract

SnO<sub>2</sub> metal oxide thin film structure modified with MWCNT was fabricated using relatively simple chemical preparation solution method and exploited as hydrogen sensor. The structural, surface morphology, topography, and electrical conductance properties of the prepared samples kept at different temperatures were investigated and explored. Although their room – temperature sensitivity was too low, the tested MWCNT – modified SnO<sub>2</sub> structures showed considerably high sensing response toward H<sub>2</sub> gas at high temperatures in comparison to the corresponding pure sensing elements. Thus, confirming the significant role of these nano structures in enhancing the semiconductor metal oxides sensing characteristics toward both oxidizing and reducing gases.

**Keywords:** Tin oxide, MWCNT's, Hydrogen Sensor, Adsorption, Sensitivity, Sensing Mechanism, S/V Ratio.

### 1. Introduction

Gas sensor is a delicate approach made to mimic one of the most significant and complicated human senses: the sense of smell. Several gas sensing methods were appeared and proposed in the scientific literature, amongst these is Semiconductor metal oxide gas sensing technique. Although numerous oxides were proposed as gas-sensor elements, like iron oxides, chromium oxides, zinc oxide, etc. Tin dioxide (SnO<sub>2</sub>) is by far the most popular semiconductor oxide used, mainly for its ability to sense hydrocarbons and carbon monoxide. SnO<sub>2</sub> is an n-type semiconductor metal oxide with a band gap of 3.6 eV, transparent, of high chemical and mechanical stability. The SnO<sub>2</sub> is used as a thin film or as a thick film sintered powder. In 1962, Naoyoshi Taguchi (Taguchi, 1962) designed the first SnO<sub>2</sub> – based semiconductor gas sensor. Thus, over 50 million Taguchi sensors have been widespread in domestic gas alarms only in Japan in the period from 1968 to 1990 (FIGARO, 1990). Nevertheless, the main drawback of this type of sensor is their lack of selectivity; for example, cross sensitivity to ethanol, carbon monoxide and methane prevents accurate hydrogen detection (Liu, *et al*, 2005).

One way to improve gas sensitivity and selectivity of a sensor includes the addition of a catalytic agent to the tin oxide powder during preparation of the sensing layer. In the case of hydrogen gas sensors, good results are obtained with the use of silver (Liu, *et al*, 2005) or palladium (GOURAI, *et al*, 1998), (Nguyen, *et al*, 2009), (Al-ansari, *et al*, 2014) and (Al-zaidi, *et al*, 2011) as additive.

Recently, much interest has been focused on carbon nanotube (CNT) as potential dopant, due to its special

electronic properties and high specific surface area that can boost catalytic reactions occurring at the metal oxide surface. Thus, the surface modification of the SnO<sub>2</sub> sensing element with CNT has greatly enhanced the sensor sensitivity and response time (S. Kumar, 2010). Ever since their first time appearance in 1991, Carbon nanotubes CNTs have fascinated scientists for the exceptional properties they possess that make them important candidate suitable for countless applications. Amongst which properties important in gas sensing include the high aspect ratio and excellent chemical and environmental stability. CNTs have the ability to detect individual reactions when a gas molecule attaches or detaches from their surface. The preliminary sensing mechanism relies on altering the charge carrier (hole, electron) density in CNTs upon being exposed to the adsorbed/desorbed gas molecules, thereby, a change in CNT resistance occurs. In addition, the electronic properties of CNTs change remarkably when exposed to a target gas. This behavior inspires the basic principle for the application of CNTs to chemiresistive gas sensors (Nguyen, *et al*, 2010), (Nguyen, *et al*, 2009)

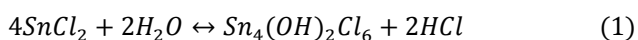
Therefore, the present study focused on the synthesis and chemiresistive characteristics of multi-walled carbon nanotubes (MWCNTs) – doped SnO<sub>2</sub> thin film sensor. The SnO<sub>2</sub> is used as the main sensing layer, while MWCNTs of small amount is utilized as a functional component to enhance the sensing performance of the main metal oxide-sensing element. The mixing of the two materials prepared by a simple chemical solution method and the thin films fabricated by dip coating method.

### 2. Experimental

#### 2.1 Preparation of the samples

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The carbon nanotubes used in this work are multi-walled carbon nanotubes prepared by a Chemical vapor deposition (CVD) method. Their diameters range from 10-30 nm, length 1-2 μm and 95% purity. A simple solution method similar to that reported by Zettl was adapted to prepare MWNT-doped SnO<sub>2</sub> (Han, *et al*, 2003). The as-received MWNTs (0.05 g) were first treated by refluxing inside a glass flask in 120 ml nitric acid (40%) at 110 °C for 2 hours to produce oxygen-containing functional groups on the sidewalls, and then washed with distilled water several times to pH = 6 and dried at 80 °C for 6 h. One gram of anhydrous SnCl<sub>2</sub>·2H<sub>2</sub>O was dissolved in 100 mL distilled water. The solution is turbid due to the hydrolysis of SnCl<sub>2</sub>, which causes the formation of Sn<sub>4</sub>(OH)<sub>2</sub>Cl<sub>6</sub> colloidal particles as follows:



HCl (38%) was added to the above solution by drop wise under stirring to suppress the hydrolysis and make it transparent. Then, 0.017 g acid treated MWCNTs were added to the solution. This mixture was sonicated for 1 h and then stirred for 30 min. at room temperature. After that, the precipitate was separated from the mother liquor by filtration and was washed with distilled water for several times, and then dried at 80 °C for 6 h. After drying, the powder product was placed in the oven at a temperature of about 500 °C. The final powder was dispersed in isopropyl alcohol C<sub>3</sub>H<sub>8</sub>O and dip coating method was used to deposit the latter solution on the porous silicon substrate and left to dry in the air at 80 °C. The prepared MWCNT-doped SnO<sub>2</sub> were characterized using x-ray diffraction (XRD), Energy-dispersive X-ray spectroscopy (EDX), scanning electron microscope (SEM) and Atomic Force Microscope (AFM). For hydrogen-sensing measurements, two Al-interdigitated electrodes IDE were thermally - evaporated onto a thin film.

## 2.2 Gas sensor testing system

The details of the gas sensor testing unit which was used in the current tests is described elsewhere (Al-zaidi, *et al*, 2011). 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 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 for 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 2×10<sup>-2</sup> 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.

## 3. Results and Discussions

### 3.1 Crystalline Structure and morphology

The structure and crystal of the film were observed by Bruker D2 PHASER XRD technique under the conditions power diffraction system with Cu-Kα X-ray tube (λ = 1.54056 Å). The x-ray scans were recorded with the diffraction angle 2θ in the 20°- 60° range. The X-ray diffraction (XRD) patterns of MWCNT-doped SnO<sub>2</sub> are shown in Fig.1. Only SnO<sub>2</sub> in the crystalline phase, including (110), (101), (200), (111), (211), (220) and (002) diffraction peaks, could be indexed from the patterns for the composite. Note that the characteristic peaks of MWCNTs could hardly be identified from the patterns of the composite. This observation could be explained by the concentration of MWCNTs, being far lower than that of SnO<sub>2</sub> matrices. Such a low MWCNT concentration could barely be detected by X-ray diffraction.

Because the MWCNT diffraction peak was not observed in the XRD, an energy-dispersive x-ray spectrometer (EDX) was done to determine the existence of MWCNTs. The EDX spectrum of the MWCNT-doped SnO<sub>2</sub> material was obtained and is shown in Fig.2. EDX spectrum shows the presence of Sn, O, Si and C which further confirms the presence of SnO<sub>2</sub> on MWNTs.

The morphology of the MWCNT-doped SnO<sub>2</sub> thin film, which was observed using Atomic force microscope AFM type (AA3000 Scanning Probe Microscope), was performed to measure the average diameter of thin films and roughness of the surface (Fig.3). Also, sample images were obtained by Scanning electron Microscope (SEM) type (Inspect<sup>TM</sup> S50) and these images are shown in Fig.4. The AFM image of the surface morphology of the thin film, shown in Fig.3-a, gives a good indication for formation of the SnO<sub>2</sub> with average particle size of about 86.59 nm. The average roughness, Ra of the sample is of the order of 5.24 nm whereas, the peak – to – valley roughness, RPV takes value of up to 25.3 nm. This result indicates that the coating surface morphology of SnO<sub>2</sub>-MWCNT thin film is almost smooth with nanosize grains. Fig.4 illustrates morphology of the thin film by scanning electron microscope (SEM). In the MWCNT-doped SnO<sub>2</sub> films, such nearly spherical SnO<sub>2</sub> particles are smoothed out and smaller grain sizes are observed. In addition, the CNTs are well embedded and randomly arranged inside the SnO<sub>2</sub> film as indicated by the yellow circles in the figure. It can be seen that although the distributions of CNTs in the films are quite random, the densities of the observed CNTs are proportional to the concentration of CNTs in the initial mixed powders. Therefore, the amount of CNTs in the film can be well controlled by varying the percentage of CNTs in the initial mixed powder.

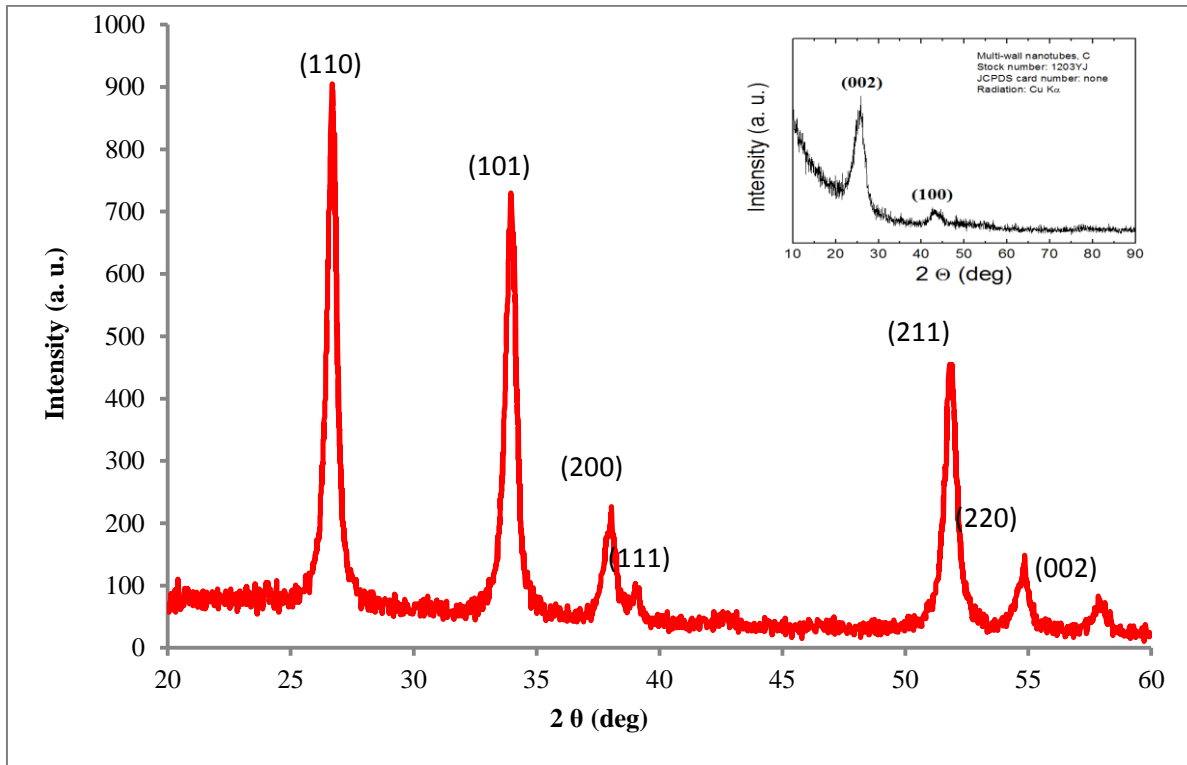


Fig.1 XRD pattern of powder MWCNT-doped SnO<sub>2</sub>. The inset shows XRD of MWCNT

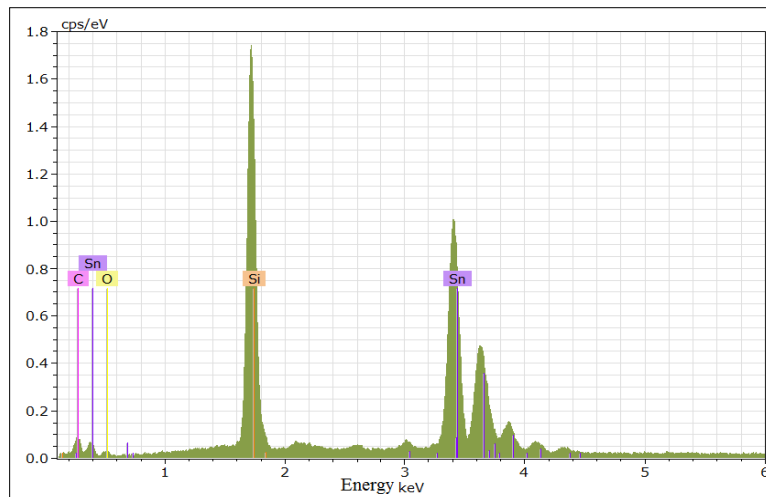


Fig.2 EDX spectrum of MWCNT-doped SnO<sub>2</sub> on porous silicon substrate

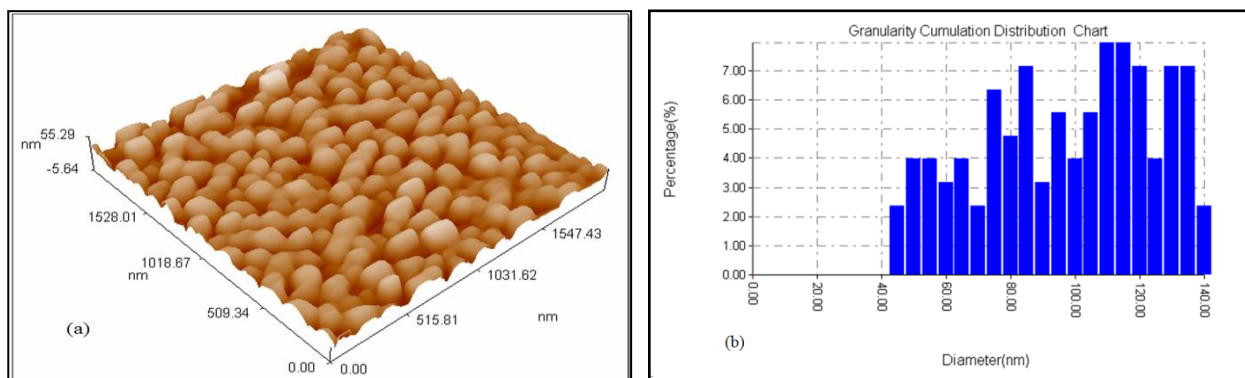
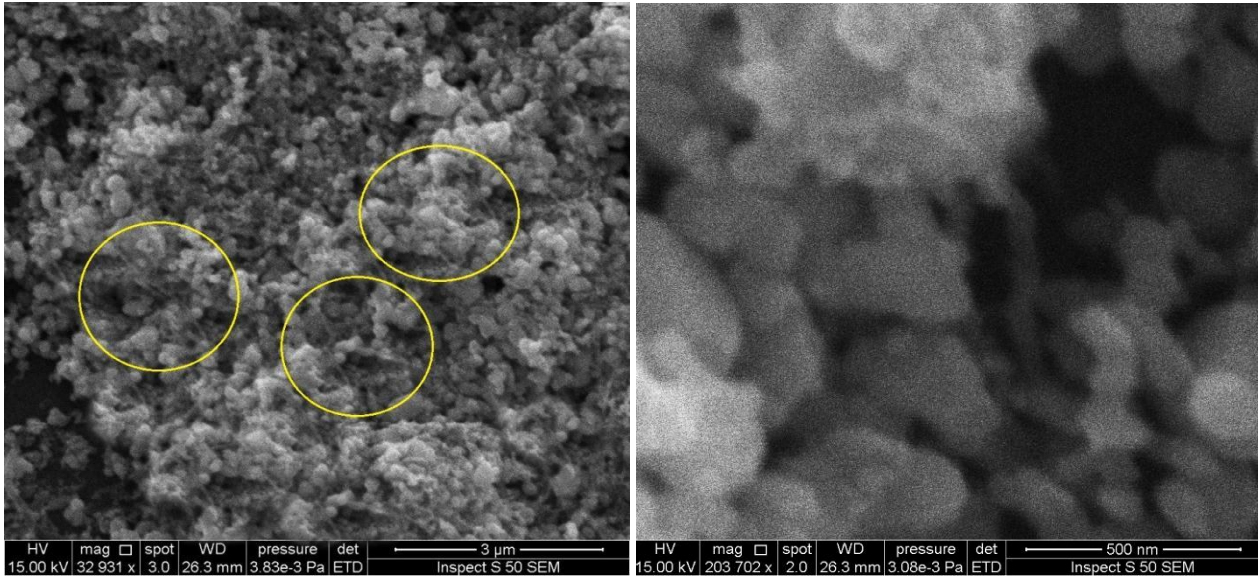


Fig.3 (a) AFM image of MWCNT-doped SnO<sub>2</sub> on Porous silicon and (b) Granularity Cumulation distribution Chart



**Fig.4** SEM images of CNT–doped SnO<sub>2</sub> film on porous silicon substrate. The yellow circles indicate CNT fragments

### 3.2 Sensing Properties

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 (Nguyen, *et al*, 2009). The response of the sensor is affected by the geometrical factor K, the electronic characteristics term of the sensing element and the adsorption induced band bending term as in the following relation, (Lupan, *et al*, 2010):

$$S = K \left( \frac{\epsilon\epsilon_0}{en_0} \right)^{1/2} (V_{Sa}^{1/2} - V_{Sg}^{1/2}) \quad (2)$$

where  $K=4/D_\lambda$  ( $D_\lambda$  is the Debye length of sensing material) and  $n_0$  is the carrier concentration in air.  $V_{Sa}$  and  $V_{Sg}$  are the absorbance-induced band bending potential in air and in H<sub>2</sub> gas, respectively. Enhancement of the sensor sensitivity to H<sub>2</sub> gas can be accomplished by controlling the above three terms via doping, modulating the operating temperature, or by altering the geometric parameters. In our work, sample doping with carbon nanotube highly increased the adsorption of hydrogen gas on the SnO<sub>2</sub> surface, and thus modulating the surface depletion region thickness through the variation of the charge carrier concentration.

Fig.5 shows the representative real – time electrical response of a 266 nm – thick MWCNT – promoted SnO<sub>2</sub> sensing element to H<sub>2</sub> gas concentration of 2.5% in air. The test was performed at various sensing temperatures with 4.8 v bias voltage.

The sensitivity S% ( $S = \left| \frac{\Delta G}{G_0} \right| \times 100\%$ ) increased with increasing operating temperature T (225 °C - 300 °C), where maximum sensitivity of 342.42% was obtained at 300 °C testing temperature after which it began to drop with increasing T and the test was terminated. This dependence of sensing response on the operating temperature of the MWCNT–SnO<sub>2</sub> film is exhibited in Fig.6. It is seen that the film maximum conductance  $G_{max}$

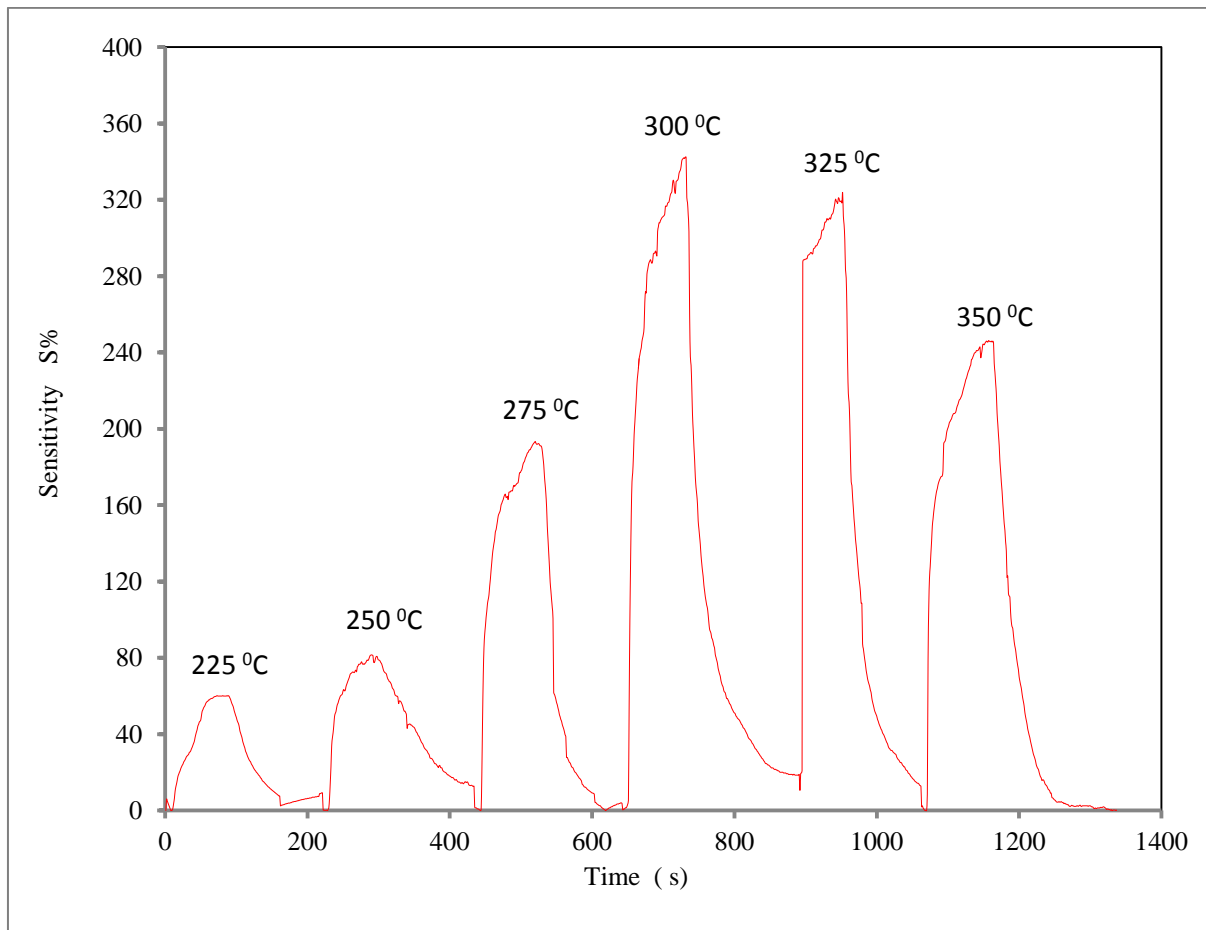
( $1/R_{max}$ ) goes through a maximum on changing T, with the best operating temperature at around 300 °C. Roughly speaking, the increase of  $G_{max}$  (the left side of the maximum) results from an increase in the rate of surface reaction of the target gas, while the decrease of  $G_{max}$  (the right 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). This explains qualitatively why the correlations between  $G_{max}$  and T take a volcano shape for semiconductor metal oxide gas sensors.

Fig.6 shows the switching behavior of the MWCNT-doped SnO<sub>2</sub> gas sensor. A relative enhancement in sensor sensitivity towards hydrogen gas is achieved in which, the sensor current increased upon being exposed to various hydrogen gas concentrations.

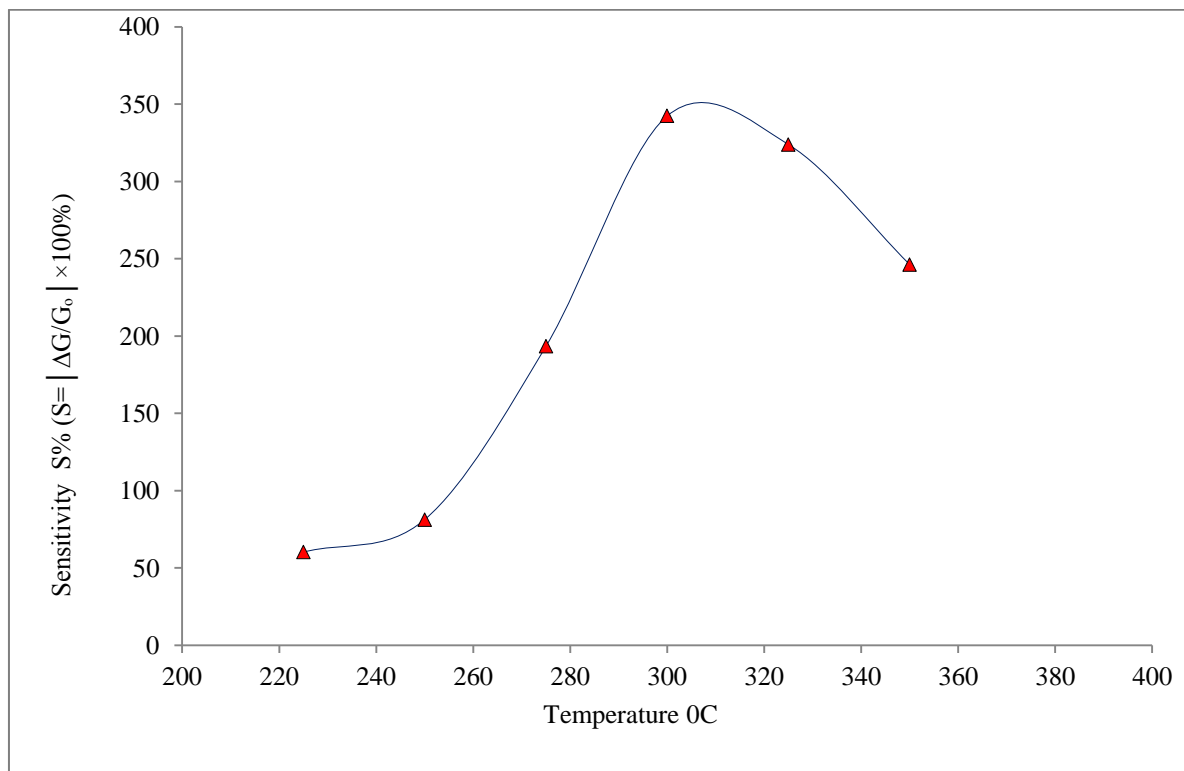
Fig.7 shows the sensitivity S variation with hydrogen gas concentration. This figure shows the sensitivity S% increased with increasing hydrogen gas concentration, where maximum sensitivity of (295.07%) was obtained in 4% hydrogen: air gas mixing ratio after which the current tends to saturate with increasing the analyte gas. A relatively short response time of about 17 s was noticed at 3.5% hydrogen gas concentration.

Fig.8 shows the sensitivity variation with hydrogen gas concentration in which the sensitivity S% increased with increasing hydrogen gas concentration. Maximum sensitivity of 295.07% was obtained at 4% hydrogen: air gas mixing ratio after which the current tended to saturate with increasing the analyte gas. A relatively short response time of about 17 s was evaluated at 3.5% hydrogen gas concentration.

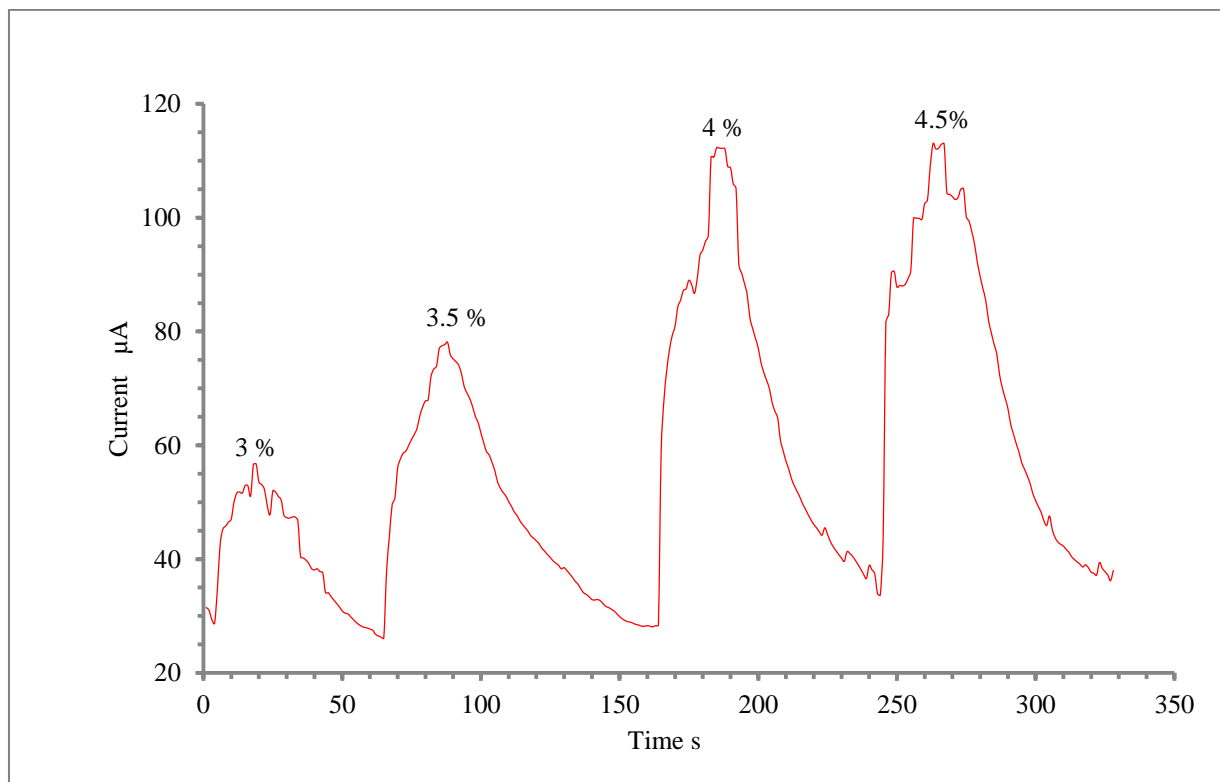
This result gives indication that one major advantage of MWCNT-doped SnO<sub>2</sub> thin film is that the sensor can be operated at a lower operating temperature (250 °C) with higher sensitivity, especially if this sensor is used to measure the H<sub>2</sub> gas at higher concentrations (3%–4.5%).



**Fig.5** Transient response of MWCNT - doped SnO<sub>2</sub> thin film of 266 nm thick at various testing temperatures upon exposure to 2.5% H<sub>2</sub>: air gas mixing ratio and 4.8 bias voltages

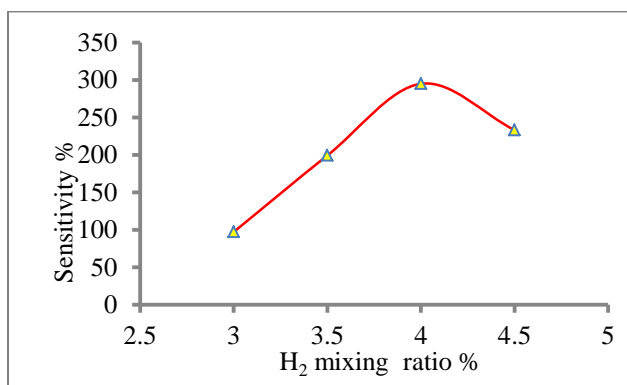


**Fig.6** Sensitivity variation with the operating temperature of the MWCNT - doped SnO<sub>2</sub> gas sensor



**Fig.7** Transient response of MWCNT – doped SnO<sub>2</sub> gas sensor to different H<sub>2</sub>: air mixing ratios. The test performed at 250 degrees temperature and 4.8 v bias voltage

At such a concentration range, shown in Fig.8, there is sufficient number of H<sub>2</sub> molecules available to react with the surface oxygen adsorption sites. It is also well-known that MWCNTs contribute to the reduction of sensor resistance of metal oxides (Hieu, *et al*, 2010) and the activation energy between the SnO<sub>2</sub> surface and H<sub>2</sub> gas.



**Fig.8** Sensitivity versus H<sub>2</sub> gas concentration of MWCNT-doped SnO<sub>2</sub> thin film. The bias voltage was 4.5 v with the temperature set to 250 °C

### 3.3 Mechanism of MWCNT-doped SnO<sub>2</sub> thin film sensor

From the gas sensing data, small percentage of CNT doping significantly enhances the sensing of H<sub>2</sub> gas. It is well known that SnO<sub>2</sub> is an n-type semiconductor while CNT is a p-type semiconductor. MWCNT-doped SnO<sub>2</sub> thin film can be either p-type or n-type semiconductors depending on the quantity of MWCNTs and the operating

temperature (Cheong, *et al*, 2006). In this work, the produced MWCNTs-doped SnO<sub>2</sub> thin film behaves as an n-type semiconductor since the electrical conductivity (current) of the film increases when reducing gases, i.e., H<sub>2</sub>, are absorbed by its surface.

The results are consistent with other reports based on CNT-SnO<sub>2</sub> composites (Wei, *et al*, 2004), (Wisitsoraat, *et al*, 2006). In these reports, various explanations for gas sensing enhancement by CNTs have been proposed. For example, amplification effect of the PN junction structure between n-SnO<sub>2</sub> and p-CNT (Wei, *et al*, 2004), the oriented growth of SnO<sub>2</sub> along the CNTs during heat treatment and its consequent enhancement of the local electric field are favorable for the gas-sensing reaction (Liu, *et al*, 2008) and increased surface area due to the formation of CNT protrusions (Wisitsoraat, *et al*, 2006).

In this work, we propose that the observed enhancement effect is attributed to the nanochannels formed by MWCNTs embedded in SnO<sub>2</sub>. The formation of the nanochannels in SnO<sub>2</sub> surface can increase the surface area and thus increase the diffusion of the gas molecules into the metal oxide surface as well as enhance local electric field at CNT-SnO<sub>2</sub> interface. The gas molecules can easily transport into the gas sensing layers leading to increasing sensitivity (Sakai, *et al*, 2001). This can considerably enhance dehydrogenation reactions of H<sub>2</sub> as described by (Lupan, *et al*, 2010):



Various oxygen species chemisorbed at the thin film surface such as O<sup>2-</sup>, O<sub>2</sub><sup>-</sup>, and O<sup>-</sup> are available for catalytic

reactions with H<sub>2</sub>, thus depending on the temperature at the metal oxide surface (Cheong, *et al*, 2006). At the operating temperature range of 150–350 °C, O<sup>-</sup> is commonly chemisorbed. The adsorbed O<sup>-</sup> on the thin film surface reacts with the H<sub>2</sub> gas yielding H<sub>2</sub>O and releasing electrons which contribute to the current increase through the thin film that causes the electrical conductivity to increase. The experimental results, particularly the sensitivity of the MWCNT-doped – SnO<sub>2</sub> – H<sub>2</sub> sensor being higher than that of the pure SnO<sub>2</sub> sensor, imply that the response of the MWCNT-doped SnO<sub>2</sub> sensor is mainly contributed by MWCNTs.

## Conclusions

Improved sensitivity of tin oxide as hydrogen sensing elements via modification with MWCNT's is realized in this study using simple SnCl<sub>2</sub> solution preparation method. Relatively high hydrogen sensitivity was achieved at the optimum operating temperature around 300 °C when compared to the pure tin oxide (SnO<sub>2</sub>). A volcano – shaped relationship is obtained between sensitivity and H<sub>2</sub>: air mixing ratio implying the sensing element surface site gets saturated with gas molecules and any increase in gas concentration causes a decline in sensitivity.

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