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Short Communication

Specific Fast Response CH_4 Gas Sensor Based on Metal Oxide, Tungsten Carbide /SnO_2Core-Shell Modified Interdigitated Electrode

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Abstract
In this study, a specific CH_4 sensor is fabricated based on interdigitated electrode that modified with core-shell of tungsten carbide/tin oxide (WC/SnO_2) nanoparticles by wet chemical method in different percents of carbon and tungsten. The morphology of wet chemical-synthesized WC/SnO_2 core-shell was evaluated by different methods such as patterned X-ray diffraction (XRD), and particle size analyzer (PSA). The fabricated sensor is selected as specific nanomaterial for CH4 detection. In the fabricated CH_4 sensor, change in resistance of the sensor was considered as the detection system. In this study, figures of merits such as linearity, specificity, response time were also evaluated. No serious interference was evaluated for different foreign gases, introduced to a certain concentration of CH_4. The reliability of the fabricated CH_4 sensor was evaluated via measuring CH4 in several gaseous samples. A fast response time about 8s and recovery time 11s has obtained from (5.0% WC-doped SnO_2).
***Keywords**: CH_4 gas sensor, SnO_2, Core-shell, Fast response time.*

1. INRODUCTION

Recently, gas sensing, as a typical application in intelligent systems, is receiving increasing attention in both industry and academia. Gas sensing technology has become more significant because of its widespread and common applications in the following areas: (1) industrial production (e.g., methane detection in mines) [1]; (2) automotive industry (e.g., detection of polluting gases from vehicles) [2]; (3) medical applications (e.g., electronic noses simulating the human olfactory system) [2-5]; (4) indoor air quality supervision (e.g., detection of carbon monoxide)[3-5];(5) environmental studies (e.g., greenhouse gas monitoring) [4]. Methane (CH_4) is major constituent of natural gas that is widely used in our daily life as prime energy-source material. This compound is much stronger green house gas compared to carbon dioxide. The explosive limit of CH_4 is ~5wt.% in air. Compared to other hydrocarbons, CH_4 has very low explosive limit [1]. Therefore, the major risk of CH_4 is an explosion hazard, which may occur if CH_4 concentration reaches its explosive limit. These all show the strong necessity of CH_4 detection and determination. During the last decade, several researchers have attempted to detect

CH_4 [2]. However, there are various types of commercial CH_4 sensors, but none of these sensors can detect CH_4 without fault.Most of these commercial CH_4 sensors are fabricated using metal oxide [2]. Semiconducting metal oxide gas sensors have attracted much attention in the field of gas sensing under atmospheric conditions due to their low cost and flexibility in production; simplicity of their use. In addition to the conductivity change of gas-sensing material, the detection of this reaction can be performed by measuring the change of capacitance, work function, mass, optical characteristics or reaction energy released by the gas/solid interaction [3]. But, high working temperature (~400 ◦C) of metal oxide-based CH_4 sensors may easily lead to explode the CH_4 [4].

Tin oxide is by far as the most key functional semiconductor oxide for gas sensing applications because of high surface-area to bulk-ratio, good chemical stability and high sensitivity at lower operating temperature, compared to other oxides for detection of reducing and oxidizing gases [5].

Tin oxide (SnO_2) is an n-type granular material whose electrical conductivity is dependent on the density of pre-adsorbed oxygen ions on its surface. The resistance of tin dioxide changes according to the variation of gas concentration such as methane (CH_4) .It is a wide band gap (Eg = 3.6 eV). Because of its excellent optical and electrical properties, SnO_2 is extensively used as a functional material for the optoelectronic devices, gas sensors, varistor, ion sensitive field effect transistors, and transparent conductive coatings for organic light emitting diodes. Radio frequency (RF) Sputtering, direct current (dc)-magnetron sputtering, thermal evaporation, ion beam deposition, spray pyrolysis, and sol-gel are the most studied methods for the preparation of SnO_2 [6-8].

Now much attention has been focused on resistive type gas sensor based on SnO_2 in practice for detecting CH_4.It can be adjusted to respond to different gases by choosing operating temperature, nanostructure modification and by the use of dopant and catalyst.

Sensing properties such as sensitivity, selectivity, working temperature can be improved by several approaches including nanoscale, crystallies, additives, etc. One of the characteristics of nanometric materials is their high surface area/volume ratio. Thesis improves the adsorption of CH_4 on the sensor and can increase the sensitivity of device because the collision between the analytes and the sensing part is higher. Various dopants such as Pd, Pt, W, Fe, WO3, etc. have been widely used to reduce response time and working temperature and sensitivity.

Cabot et al. studied [9] a correlation between the catalytic activity and the sensor response of different modified SnO_2 samples to CH_4 as target gas. It was found that, the catalytic oxidation of methane is more pronounced for Pd than Pt.

JiptoSujitno and Sudjatmoko also found that, the influence of platinum dopant on SnO_2 thin film can reduce significantly the resistance of thin film. Also, different response time and sensitivity were evaluated during different replicated fabrication of sensor [10].

Thin films of undoped and 0.1wt.% Ca-doped SnO_2 with 30–60 ˚A Pt layers deposited by ion beam sputtering have been structured on Si substrates. CH_4 sensitivities for those Pt.-covered undoped and Ca-doped SnO_2 sensors are compared in terms of root-mean-square surface roughness's measured by Bong-Ki Min et al [15].

CH_4 gas sensors made of the nanocomposites of Sn/In/Ti oxides were investigated by BaiShoulia et al. The sensing tests showed that these nanocomposites exhibited high response and selectivity for the detection of CH_4 at operating temperatures between 200-250 ◦C [11].

In this study, a specific CH_4 sensor is fabricated based on interdigitated electrode on SiO_2 that modified with core-shell of tungsten carbide/tin oxide (WC/SnO_2) by

wet chemical method. Compared to previously reported CH_4 sensor [4], the fabricated sensor has significant novelties such as specificity, reproducibility, high sensitivity, more improved detection limit and short response time.

2. EXPERIMENTAL

2.1. Preparation of sensing materials

Tungsten powder (99.9%) was first dissolved in 30wt.% H_2O_2 to give a 3.0 M solution of tungsten, which was used as the source of tungsten for the synthesis of the carbide. The tungsten solution with added SnO_2 and carbon was stirred for 30min with 200±2 rpm speed and stayed at room temperature for 24 h. The solution was sonicated for 15min then was centrifuged and obtained powder was introduced to the CVD instrumentation system that was handmade, for core-shelling on SnO_2. It was followed by flowing a mixture of Ar and H_2 gases with Ar/H_2 volume ratio of 10 through the SnO_2 at 700 °C for ~3h.this mixure played the role of catalyst to create WC-doped SnO_2. Finally, the temperature was decreased to room temperature with a cooling rate of 5 °C min^{-1}.Obtained samples was in different proportion of SnO_2, W and C as follows:

Sample Number	Compound
1	Undoped SnO_2
2	5.0% *(wt)* WC doped SnO_2
3	10.0% *(wt)* WC doped SnO_2
4	50.0% *(wt)* WC doped SnO_2

2.2. Characterization of sensing materials

Figure 1 shows the XRD pattern of WC doped SnO_2 and W doped SnO_2 nanopowder. Morphologies of SnO_2 and tungsten carbides (WC, W_2C) are clearly shown in Figure. 1. To determine the particle size of components, particle size analyzer (PSA Horiba-LB 550) used as shown in Fig. 2 .According to Fig.2 the size of sample #2 is approximately 140nm (Figure. 2(a)) and the size of sample #3 is obtained ~300nm as shown in Fig. 2(b) . Also Figure. 3 presents the "Scanning Electron Microscopic" (SEM) images of samples. Figure 3(a) shows the SEM image of undoped SnO_2 and also the core-shell structure of 5.0% WC doped SnO_2 is observed in Figure. 3(b)

2.3. Measurement of sensor response

The sensitivity of samples in the presence of methane was tested inside test chambers that measure the change in surface resistance of the samples on gas exposure as shown in Figure.4. The sensing unit in Fig. 4 includes gold interdigitated electrodes on SiO_2 substrate that sensing materials are coated on electrodes. After coating the sensing materials, they are sintered in the temperature of 250-500°C.
The sensitivity is defined as:

$$S= (R_{gas} - R_{air}) / R_{air} \quad (1)$$

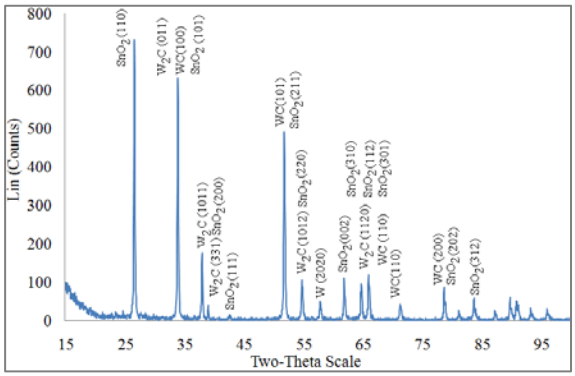
Where R_{air} and R_{gas} are the resistance of the sensor in air and gas at the same temperature.

3. GAS SENSING

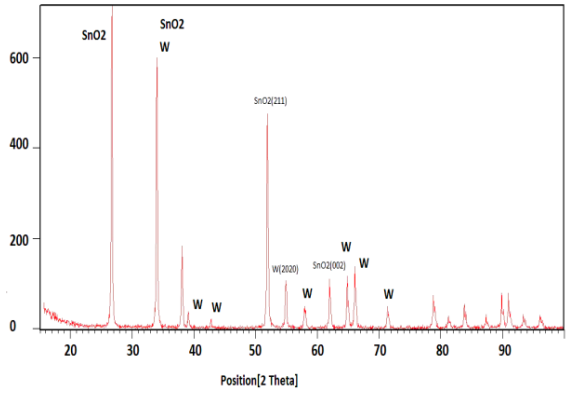
3.1. Mechanism of sensing

The electronic effect of the adsorption of CH_4 on the SnO_2 surface can be described by the band structure model. The fundamental conduction model of metal oxide has been discussed in details in [17]. In the following, the electronic structure of the semiconductor and changes of its band structure by adsorption processes will be described. For simplification, the influence of the adsorption processes on the electronic band structure will be shown on the basis of oxygen adsorption. Figure.5 shows the sensing mechanism of this SnO_2 type methane sensor. SnO_2 is an n-type semiconductor with electrons as the

majority carriers. In air, the conductance value reduces due to the chemisorptions of oxygen, but in presence of reducing gas such as methane, the chemisorbed oxygen reacts with the methane to increase the electrical conductance.



(a)



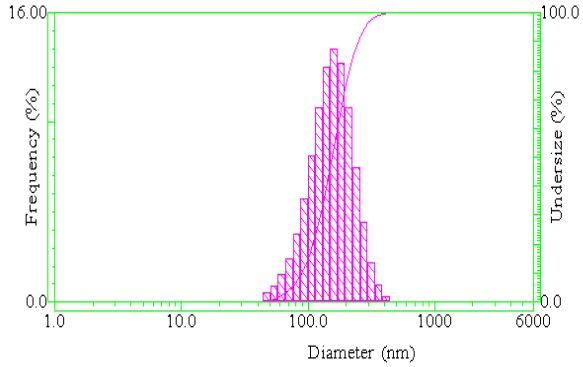
(b)

Figure1. *XRD patterns of SnO_2 thin film including (a) WC-SnO_2 and (b) W-SnO_2.*

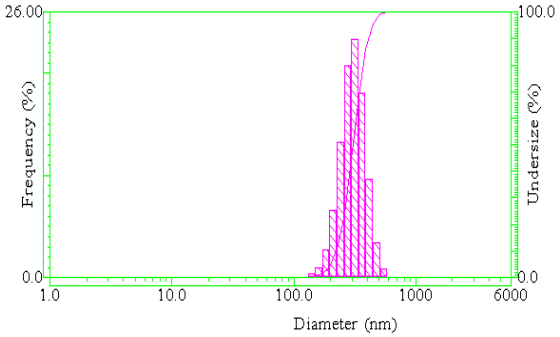
Whereas the electrical conductance of WC doped SnO_2 decreases in presence of methane because WC (tungsten carbide) is a p-type and SnO_2 is an n-type semiconductor when they interact with each other the potential difference between WC and SnO_2 neutral region is:

$$\psi_0 = \psi_n - \psi_p = \varphi_T \ln N_d N_a / n_i^2 \quad (2)$$

Where N_d , N_a are donor and acceptor concentration. In Fig. 6 with sensing CH_4, N_d related to SnO_2 increases and cause to increasing ψ_0. Therefore, the electrical conductance of WC doped SnO_2 decreases in opposite of undoped SnO_2.



(a)



(b)

Figure2. *Histograms showing the size distribution of (a)5%WC/$SnO_2$and(b)10%WC/SnO_2 thin film.*

The sensitivities of various samples to CH_4 were measured over an operating temperature range of 90–300 ˚C and correlated with their composition and operating temperature. The sensitivity data are presented in Fig.8. These results indicate that the 5.0%WC doped.

4. RESULTS AND DISCUSSION

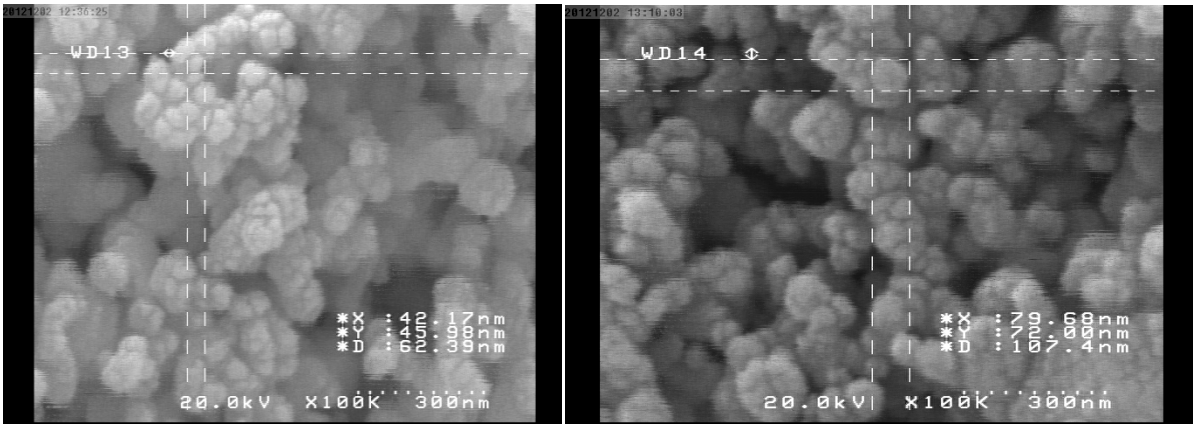
4.1. Sensor Response to CH_4

In this work, the static and dynamic responses of sensor are studied. All sensing materials that are dispersed in ethanol are tested with exposing methane. One of the disadvantages of the semiconductor-based sensors is that, they are usually operated at moderate temperature between 300-400 °C. Operating temperature is defined as temperature at which the resistance of the sensor reaches the constant value. This is due to fact that, change in the resistance is

justly influenced by the presence of amount of CH_4 gas [10].

Compared to the previously reported CH_4 sensors, the fabricated sensor operates at lower temperatures between 180-270 ^oC. The results are shown in Figure. 7. As clearly evaluated based on the Figure. 7, significant lowering is observed in the background resistance of the sensor at temperature below 250 ^oC.

SnO_2nanocompositecalcined at 600 ◦C has the largest response value of 10 to 5000 parts per million (ppm) CH_4 at 200 ◦C; thus, it is the optimum composite for the detection of CH_4as shown in Figure.



(a) ***(b)***

Figure3*. SEM images of different samples including (a) undoped $SnO_2$and (b) 5.0%WC- SnO*

This sample (#2) has the largest sensitivity value at T=200◦C that operated at lower temperature than other reported works on metal oxides gas sensors. It is an advantage for this composite.

According to the Figure.9 maximum sensitivity value is belong to 5.0 %WC doped SnO_2 at T=200 ℃ for 10000ppm CH_4. It can be seen from this Figure that increasing in the operating temperature to 270 ºC cause to decreasing in sensitivity value of WC doped SnO_2 from 10 to 6.

4.2 Type of materials sensing conductivity

The variation from undoped SnO_2 to WC-doped SnO_2 shows the potential in obtaining different semiconductor types (n-type and p-type).So as adding tungsten carbide (WC) has been caused that n-type SnO_2 convert to p-type WC-SnO_2. From Fig.10, it can be seen that, during the CH_4injection, the resistance decreases due to n-type conductivity of SnO_2, but in Fig.11 on exposure to CH_4, the resistance of WC-SnO_2 increases rapidly because WC-SnO_2 is p-type. This change of semiconductor type cause improvement in behavior sensor.

Here, to ensure the sensor response to CH_4, not to the pressure of the gas inlet is changed in the absence of CH_4 gas, but also the pressure of Ar gas is doubled up during the time interval. In accordance with Fig. 12, it can be seen that, the electrical resistance has approximately constant process.

4.3. Limit of Detection

Figure.13 shows that this sensor with 5%WC-SnO_2 compound can detect 100ppm CH_4at T=120 ºC with sensitivity value equal to ~4%.

Figure.13. Response of 5%WC doped SnO_2 to 100ppm CH_4 at operating temperature T=120 ºC.

However, in the present work, it was found that all the four SnO_2 sensors showed an ultra-fast reversible response at low temperature with a recovery time t_{90}%

shorter than 60 s. The results indicate that the different samples can affect the sensitivity, and have a great effect on the response time of the sensors as sample#2 is the fastest sensor that shows an ultra-fast reversible sensor at low temperature(T=120℃).

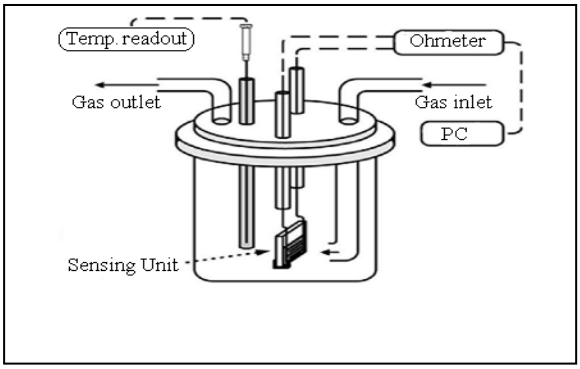


Figure4*. Gas sensing set up.*

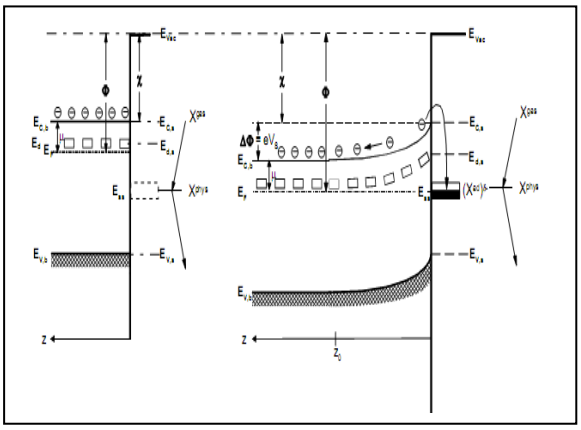


Figure5. *Electronic structure of semiconductor before and after gas adsorption on the surface. Band bending of a n-type semiconductor.[17]*

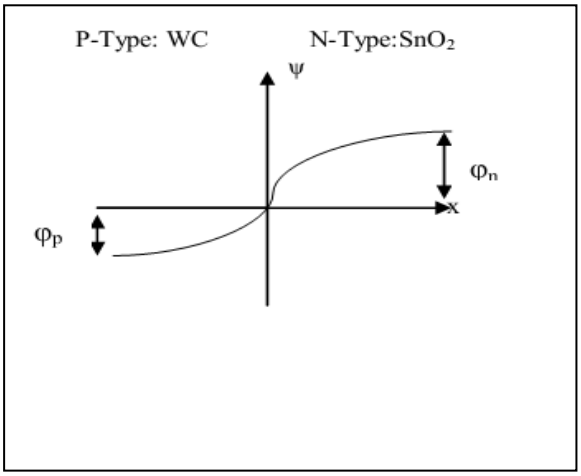


Figure6*. The step pn junction: potential diagrams.*

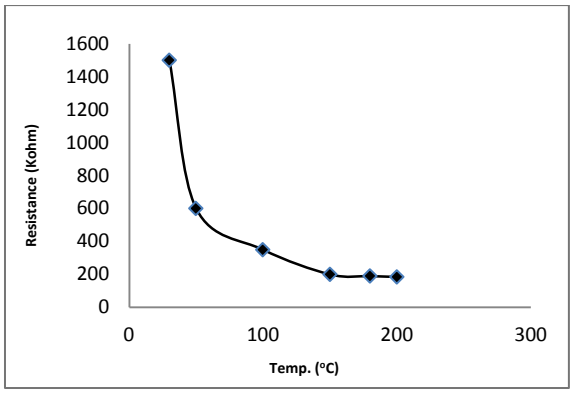


Figure7*. Effect of temperature on the resistance of SnO_2 thin film.*

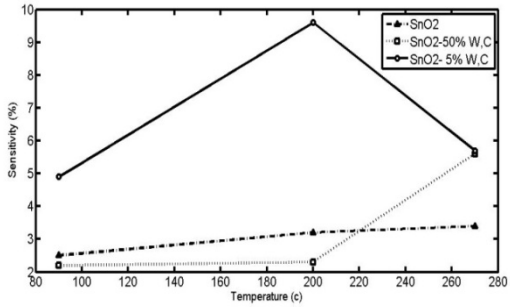


Figure8*. Response of various nanocomposites to 5000ppm CH_4 at different operating temperature.*

There are very few reports on metal oxide-based methane gas sensors with high response and shorter response and recovery time. So far the reported sensor structures based on oxide semiconductors and operating in the resistive mode at high temperature showed relatively longer response (>10 s) and recovery (>40 seconds) time for CH_4 sensing. In this investigation, particularly the WC doped SnO_2 sensor shows short response time (~22s), and recovery time (~17s) as compared to the values reported by others [14-17].

4. CONCLUSION

In summary, we used SnO_2 and WC/SnO_2 thin film for specific detection of methane. Compared to previously reported methane sensor, the fabricated sensor has significant novelties such as specificity,

reproducibility, high sensitivity, more improved detection limit and short response time.

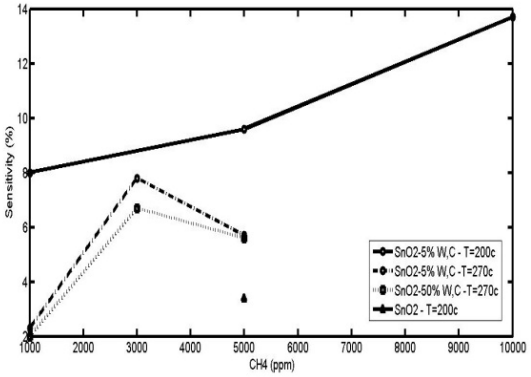


Figure.9. *Response of various nanocomposite to different concentration of CH_4 at operating temperature T=200 ℃ , 270 ℃.*

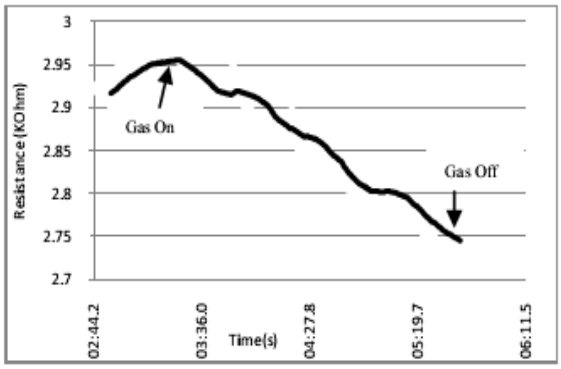
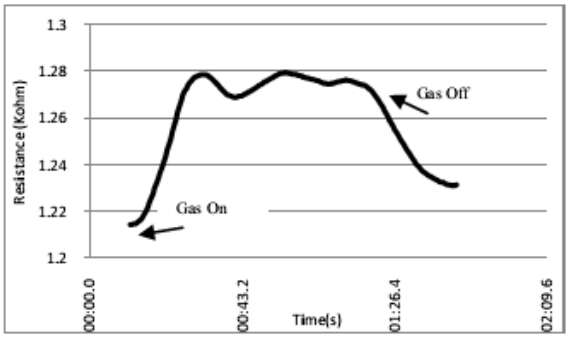


Figure10*: Response of undoped SnO_2 to 5000ppm methane at T=270 ºC.*



Figur11*: Response of 5%WC doped SnO_2 to 5000ppm methane at T=270 ºC.*

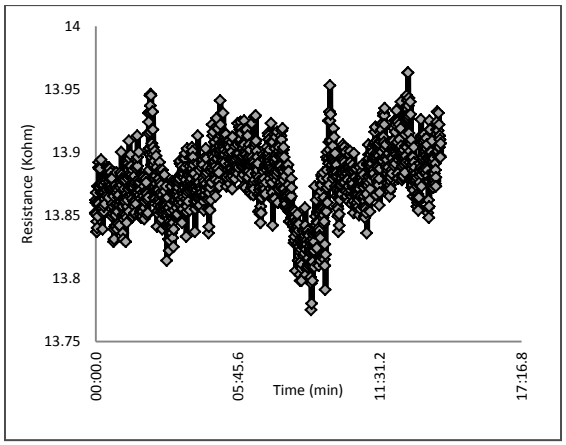


Figure12*: Response of sensor to pressure change of Ar in the absence of CH_4.*

Table1. *Response and Recovery time of our sensors and others.*

Sample Number	**Response Time (s)**	**Recovery Time (s)**	**Sensitivity**	**Temp.**
1- Undoped SnO_2	65	56	3.5%	200℃
2- 5%WC-SnO_2	22	17	14%	120℃
3- 10%WC-SnO_2	34	29	18%	200℃
4- 50%WC-SnO_2	45	38	5.6%	200 ℃
Other Works				
SnO_2 (Mosadegh sedghi et al.[16])	-	-	0	200 ℃
SnO_2(B.K.Min et al. [15])	-	-	1%	250℃
SnO_2(K.Großman et al. [13])	<40	680	-	300 ℃
0.01%Sb-SnO_2 (K.Großman et al.[13])	80	560	-	300 ℃
0. 1%Sb-SnO_2 (K.Großman et al. [13])	<40	600	-	300 ℃
3%Sb-SnO_2 (K.Großmann et al. [13])	80	>1200	-	300 ℃

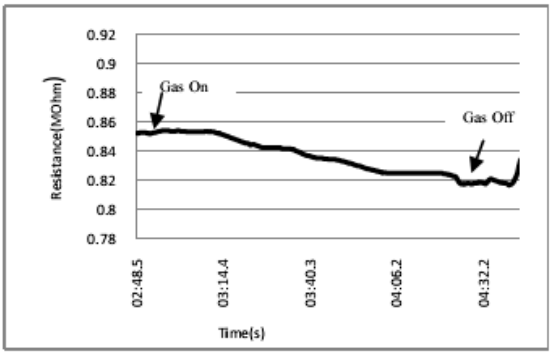


***Figure13**: Response of 5%WC doped SnO_2 to 100ppm CH_4 at operating temperature T=200 ºC.*

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