

Short Communication

Specific Fast Response CH₄ Gas Sensor Based on Metal Oxide, Tungsten Carbide /SnO₂Core-Shell Modified Interdigitated Electrode

S.Nikmanesh^{1*}, M.M.Doroodmand² and M.H.Sheikhi¹

1. School of Electrical and Computer engineering, Shiraz University, I. R. Iran

2. Department of Chemistry, College of Sciences, Shiraz University, I. R. Iran

(*) Corresponding author: nikmanesh@shirazu.ac.ir

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Abstract

In this study, a specific CH₄ sensor is fabricated based on interdigitated electrode that modified with core-shell of tungsten carbide/tin oxide (WC/SnO₂) nanoparticles by wet chemical method in different percents of carbon and tungsten. The morphology of wet chemical-synthesized WC/SnO₂ 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 CH₄ 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 CH₄. The reliability of the fabricated CH₄ 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 SnO₂).

Keywords: CH₄ gas sensor, SnO₂, Core-shell, Fast response time.

1. INTRODUCTION

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 (CH₄) 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 CH₄ is ~5wt.% in air. Compared to other hydrocarbons, CH₄ has very low explosive limit [1]. Therefore, the major risk of CH₄ is an explosion hazard, which may occur if CH₄ concentration reaches its explosive limit. These all show the strong necessity of CH₄ detection and determination. During the last decade, several researchers have attempted to detect

CH₄ [2]. However, there are various types of commercial CH₄ sensors, but none of these sensors can detect CH₄ without fault. Most of these commercial CH₄ 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 CH₄ sensors may easily lead to explode the CH₄ [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 (SnO₂) 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 (CH₄). It is a wide band gap (E_g = 3.6 eV). Because of its excellent optical and electrical properties, SnO₂ 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 SnO₂ [6-8].

Now much attention has been focused on resistive type gas sensor based on SnO₂ in practice for detecting CH₄. 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, crystallites, additives, etc. One of the characteristics of nanometric materials is their high surface area/volume ratio. This improves the adsorption of CH₄ 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 SnO₂ samples to CH₄ 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 SnO₂ 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 SnO₂ with 30–60 °A Pt layers deposited by ion beam sputtering have been structured on Si substrates. CH₄ sensitivities for those Pt.-covered undoped and Ca-doped SnO₂ sensors are compared in terms of root-mean-square surface roughness's measured by Bong-Ki Min et al [15].

CH₄ gas sensors made of the nanocomposites of Sn/In/Ti oxides were investigated by BaiShouli et al. The sensing tests showed that these nanocomposites exhibited high response and selectivity for the detection of CH₄ at operating temperatures between 200-250 °C [11].

In this study, a specific CH₄ sensor is fabricated based on interdigitated electrode on SiO₂ that modified with core-shell of tungsten carbide/tin oxide (WC/SnO₂) by

wet chemical method. Compared to previously reported CH₄ 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.% H₂O₂ 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 SnO₂ 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 SnO₂. It was followed by flowing a mixture of Ar and H₂ gases with Ar/H₂ volume ratio of 10 through the SnO₂ at 700 °C for ~3h. this mixture played the role of catalyst to create WC-doped SnO₂. Finally, the temperature was decreased to room temperature with a cooling rate of 5 °C min⁻¹. Obtained samples was in different proportion of SnO₂, 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 SnO₂ and W doped SnO₂ nanopowder. Morphologies of SnO₂ and tungsten carbides (WC, W₂C) 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 SnO₂ and also the core-shell structure of 5.0% WC doped SnO₂ 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 SiO₂ 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:

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

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 CH₄ on the SnO₂ 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 SnO₂ type methane sensor. SnO₂ 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.

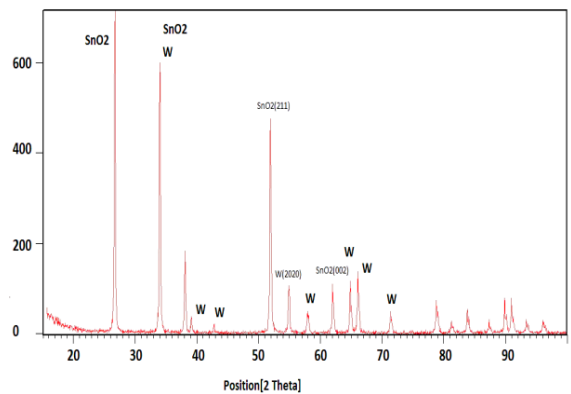
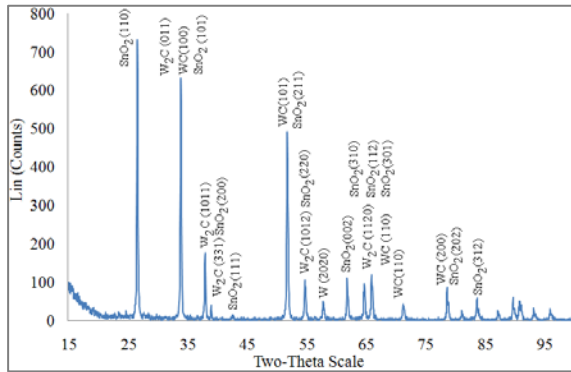


Figure1. XRD patterns of SnO₂ thin film including (a) WC-SnO₂ and (b) W-SnO₂.

Whereas the electrical conductance of WC doped SnO₂ decreases in presence of methane because WC (tungsten carbide) is a p-type and SnO₂ is an n-type semiconductor when they interact with each other the potential difference between WC and SnO₂ 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 CH₄, N_d related to SnO₂ increases and cause to increasing ψ_0 . Therefore, the electrical conductance of WC doped SnO₂ decreases in opposite of undoped SnO₂.

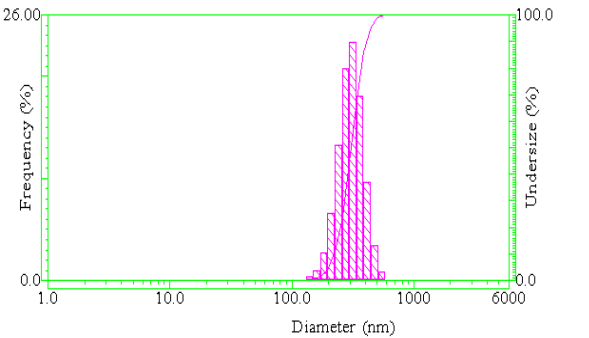
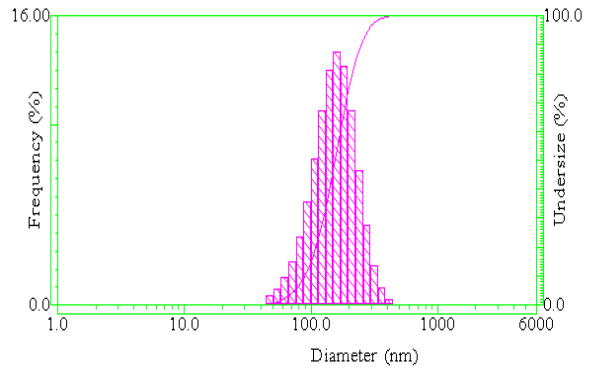


Figure2. Histograms showing the size distribution of (a) 5% WC/SnO₂ and (b) 10% WC/SnO₂ thin film.

The sensitivities of various samples to CH₄ 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 CH₄

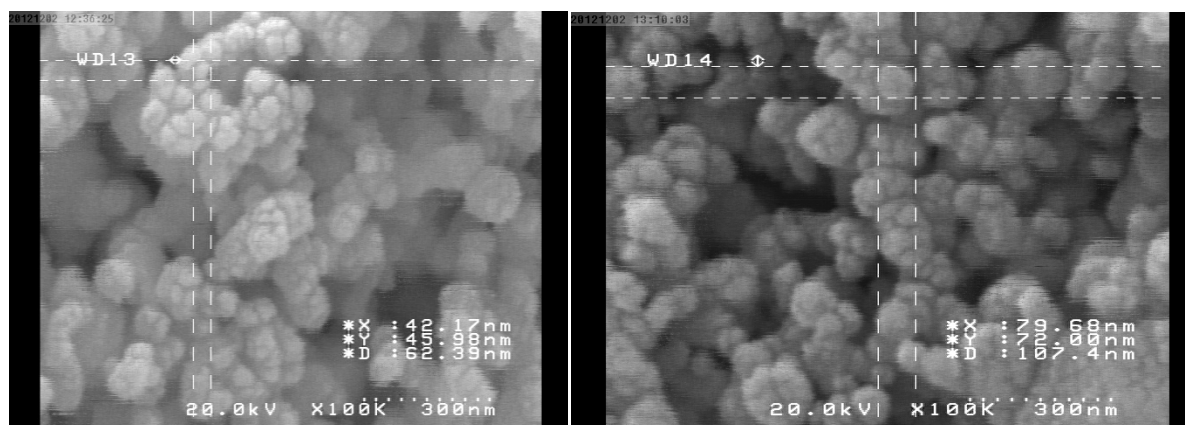
In this work, the static and dynamic responses of sensor are studied. All sensing materials that are dispersed in ethanol are tested with exposing methane. One of the disadvantages of the semiconductor-based sensors is that, they are usually operated at moderate temperature between 300-400 °C. Operating 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 CH₄ gas [10].

Compared to the previously reported CH₄ sensors, the fabricated sensor operates at lower temperatures between 180-270 °C. 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 °C.

SnO₂nanocompositecalcined at 600 °C has the largest response value of 10 to 5000 parts per million (ppm) CH₄ at 200 °C; thus, it is the optimum composite for the detection of CH₄as shown in Figure.



(a)

(b)

Figure3. SEM images of different samples including (a) undoped SnO₂and (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 SnO₂ at T=200 °C for 10000ppm CH₄. It can be seen from this Figure that increasing in the operating temperature to 270 °C cause to decreasing in sensitivity value of WC doped SnO₂ from 10 to 6.

4.2 Type of materials sensing conductivity

The variation from undoped SnO₂ to WC-doped SnO₂ 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 SnO₂ convert to p-type WC-SnO₂. From Fig.10, it can be seen that, during the CH₄injection, the resistance decreases due to n-type conductivity of SnO₂, but in Fig.11 on exposure to CH₄, the resistance of

WC-SnO₂ increases rapidly because WC-SnO₂ is p-type. This change of semiconductor type cause improvement in behavior sensor.

Here, to ensure the sensor response to CH₄, not to the pressure of the gas inlet is changed in the absence of CH₄ 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-SnO₂ compound can detect 100ppm CH₄at T=120 °C with sensitivity value equal to ~4%.

Figure.13. Response of 5%WC doped SnO₂ to 100ppm CH₄ at operating temperature T=120 °C.

However, in the present work, it was found that all the four SnO₂ sensors showed an ultra-fast reversible response at low temperature with a recovery time t₉₀%

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 ($T=120^{\circ}\text{C}$).

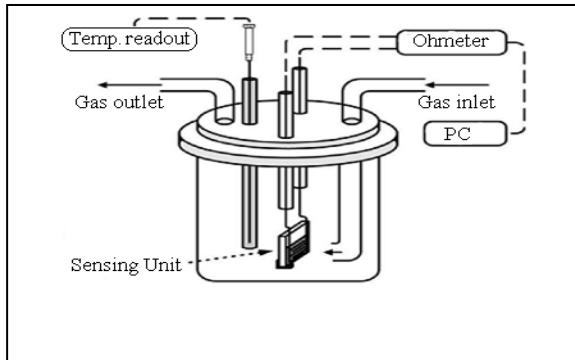


Figure 4. Gas sensing set up.

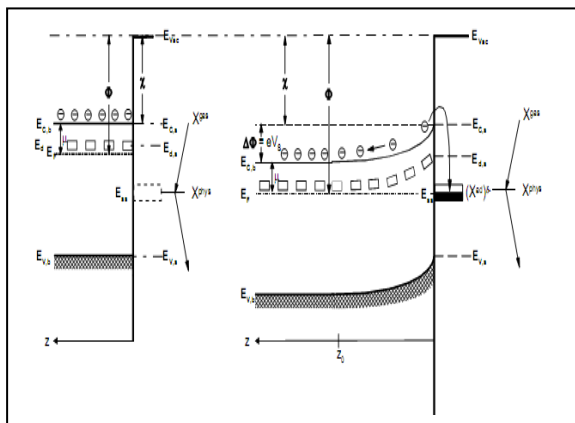


Figure 5. Electronic structure of semiconductor before and after gas adsorption on the surface. Band bending of a n-type semiconductor. [17]

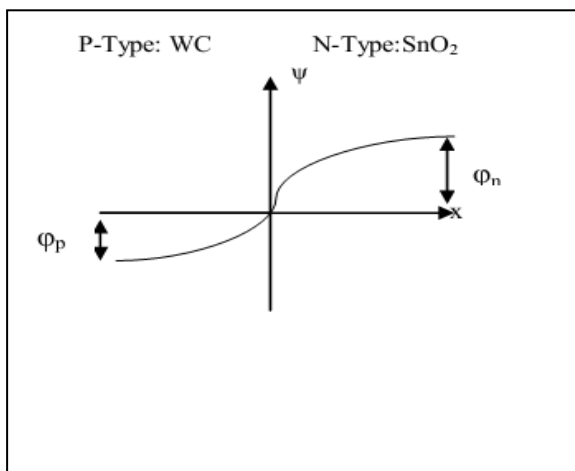


Figure 6. The step pn junction: potential diagrams.

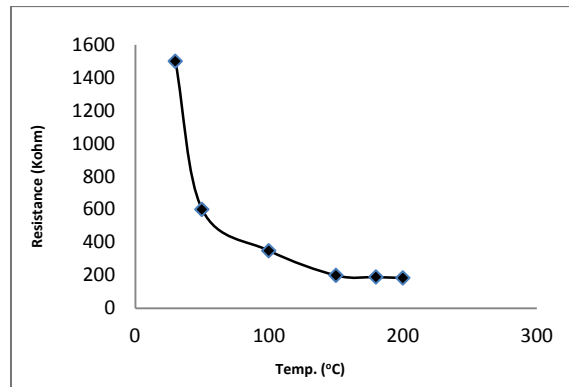


Figure 7. Effect of temperature on the resistance of SnO_2 thin film.

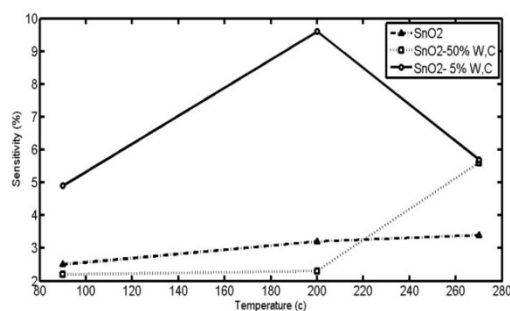


Figure 8. Response of various nanocomposites to 5000ppm CH_4 at different operating temperature.

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 ($\sim 22\text{s}$), and recovery time ($\sim 17\text{s}$) 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.

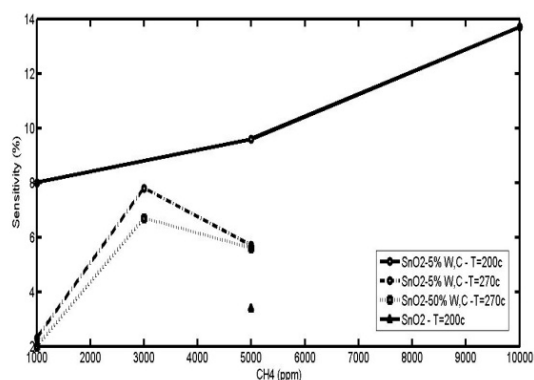


Figure.9. Response of various nanocomposite to different concentration of CH_4 at operating temperature $T=200^\circ C$, $270^\circ C$.

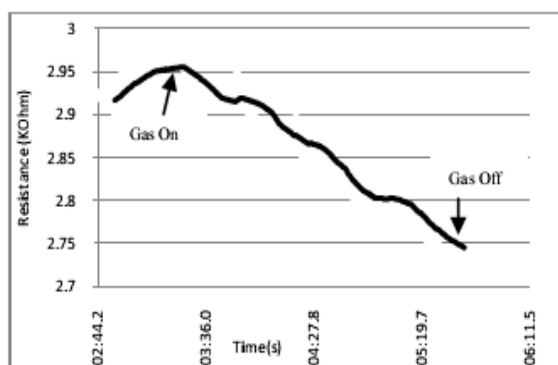
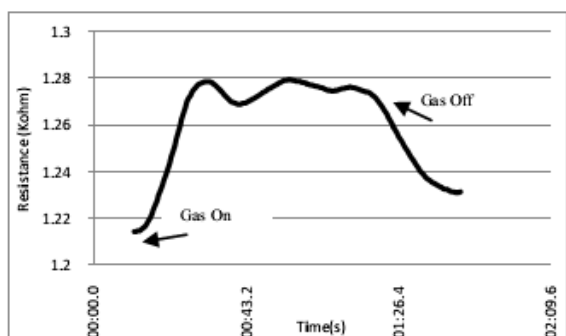


Figure10: Response of undoped SnO_2 to 5000ppm methane at $T=270^\circ C$.



Figur11: Response of 5%WC doped SnO_2 to 5000ppm methane at $T=270^\circ C$.

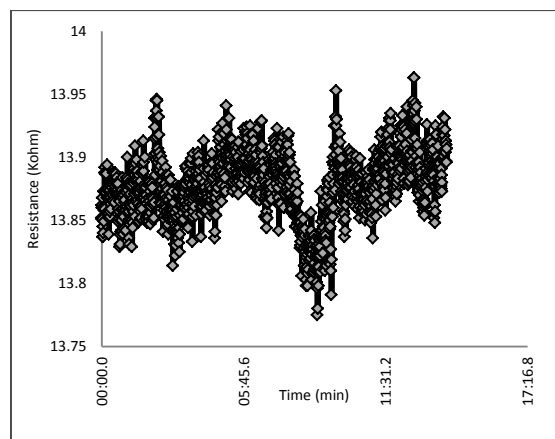


Figure12: Response of sensor to pressure change of Ar in the absence of CH_4 .

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%	$200^\circ C$
2- 5% WC- SnO_2	22	17	14%	$120^\circ C$
3- 10% WC- SnO_2	34	29	18%	$200^\circ C$
4- 50% WC- SnO_2	45	38	5.6%	$200^\circ C$
Other Works				
SnO_2 (Mosadegh sedghi et al.[16])	-	-	0	$200^\circ C$
SnO_2 (B.K .Min et al. [15])	-	-	1%	$250^\circ C$
SnO_2 (K.G roßman et al. [13])	<40	680	-	$300^\circ C$
0.01% Sb- SnO_2 (K.Großman et al.[13])	80	560	-	$300^\circ C$
0.1% Sb- SnO_2 (K.Großman et al. [13])	<40	600	-	$300^\circ C$
3% Sb- SnO_2 (K.Großman et al. [13])	80	>1200	-	$300^\circ C$

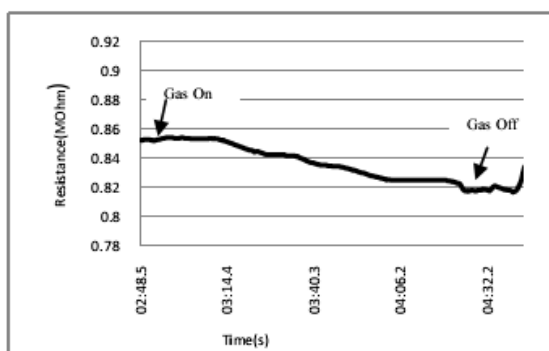


Figure13: Response of 5%WC doped SnO_2 to 100ppm CH_4 at operating temperature $T=200\text{ }^\circ\text{C}$.

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