International Journal of Recent Technology and Engineering (IJRTE)
ISSN: 2277-3878 (Online), Volume-9 Issue-1, May 2020

Analysis on Sensitivity of Semiconductor Methane Gas Sensors by Ultrasonic Process

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Abstract*: The thin films of Pt and Zn were coated with on the electrode in the board. Thin films of Pt are fabricated by ion plasma and Zn is manufactured by DC sputtering methods. Then the deposited boards were produced by ultrasonic chemical deposition in 0.01 M aqueous solution of C6H12N4 and Zn(NO3)2·6H2O. To make the ZnO prepared-substrates were heat-treated at 600 ℃ for 1 hour and the sensitivity of ZnO-structured sensors was tested for Methane gas. In the experiment, the concentrations of Methane gas ranged from 15% to 40% LEL. We measured the change of the voltage before and after the Methane gas injections to judge whether it had a suitable performance as the Methane gas sensors. As a result of the sensitivity of the fabricated sensor, it was found that the voltage increases according to the Methane concentration. The sensitivity of the sensor constantly increased, so the graph showed a linear shape. Also, the fabricated sensors showed very short stabilization time, fast reaction and recovery. As a result, the using possibility of the detector is suggested where detection is required.

***Keywords*: Heat-treatment, ZnO, Nano-structure, Sensitivity, Methane gas, Ultrasonic chemical deposition**

I. INTRODUCTION

Methane, CH4, is a colorless, odorless gas which is widely distributed in nation. As a hydrocarbon-based gas composed of carbon and hydrogen, Methane is the main component of the natural gas (LNG) and is used as fuel gas in residential and industrial fields. Methane gas explodes when the concentration in the air reaches 50,000ppm or higher. Therefore, this gas may cause a large fire of damage to human life, so it needs to be managed at all times [1].

Manuscript received on April 02, 2020.
Revised Manuscript received on April 15, 2020.
Manuscript published on May 30, 2020.
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In the last decade, gas sensors have attracted substantial interest thanks to the reasonable price, flexible production, simple application, a wide variety of detectable gases, and potential for the gas detector. ZnO-based materials are used in gas sensors because of their numerous benefits, such as good sensitivity and so on [2].

The sensing method of the semiconductor gas sensor for the target gases using high temperatures (300~400 °C) and the surface properties changes because of the conductivity of the electron exchange of gas when gas is absorbed into the surface of ZnO semiconductor. ZnO is a very useful material of a 2-6 compound semiconductor having a structured hexagonal crystal called wurtzite, direct transition band gap energy is 3.37eV, and is a ZnO-structured sensor having 60 meV exciton binding energy [3].

ZnO-structured semiconductor gas sensors have a large surface area. In order to adsorb as much Methane gas as possible into the sensor's surface area, stronger and more measurable sensitivity is required [4-6].

In this paper, we developed a methane gas sensor that can be used for the Methane gas detector installed in the plant. To manufacture the Methane gas sensor, first of all, Al2O3 substrates which were Ion-coated with the Pt and Zn film were deposited for the Zinc seed layer on each side prepared. Pt and Zn films were fabricated by ion plasma and DC sputtering deposition equipment, respectively. In addition to turning the deposited zinc powder into ZnO gas sensors were heat-treated at 600 °C for one hour. Then, the gas sensors of ZnO-structure were manufactured by ultrasonic process in an aqueous solution of 0.01 M [7-12].

In the experiment, the concentrations of Methane gas ranged from 15% to 40% LEL. We measured the change of the voltage before and after the Methane gas injections to judge whether it had a suitable performance as the Methane gas sensors. As a result of the sensitivity of the fabricated sensor, it was found that the voltage increased according to the Methane concentration. The sensitivity of the sensor constantly increased, so the graph showed a linear shape. Since the sensitivity and response speed about the methane gas are positive, it is also possible to develop sensors for natural gas.

II. EXPERIMENTAL METHOD

A. The fabrication of sensor's substrate

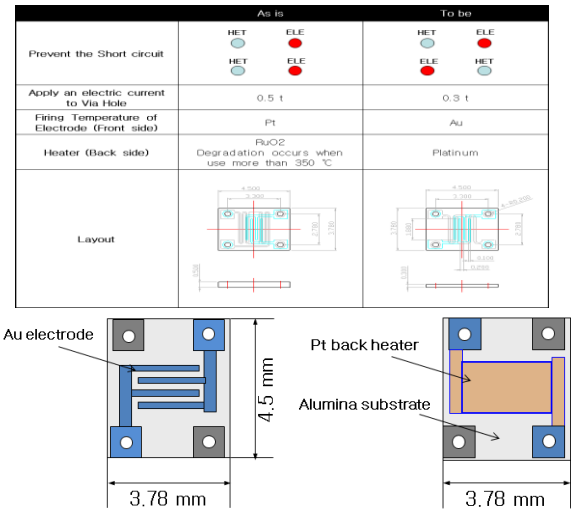

Fig. 1. Fabrication of Sensor's Substrate(Figure 1)

The size of the sensor's substrate is 4.5 mm ×3.78 mm×0.3 t. It consists of gold electrodes and an Al2O3 substrate. The resistance of platinum heater (back side) is approximately 15 Ω. To prevent short circuit, the electrodes have positioned the holes in the semiconductor Methane gas sensors. In the newly developed substrate, the short circuit has been improved by changing the positions of the sensing unit and the heater unit.

Table- I: Types and Characteristics of ZnO Nanostructure Synthesis

Category	Growth techniques	Characteristics
Vapor phase approach	**CVD** **MOCVD** **PLD**	▸ Advantages 1. Easy on-substrate growth of ID ZnO nanostructure 2. High crystallinity and ease morphology control ▹ Disadvantages 1. High reaction temperature and low pressure 2. Complicated equipment due to heating and vacuum system 3. High-cost manufacturing process
Solution phase approach	**Hydrothermal synthesis**	▸ Advantages 1. Low reaction temperature 2. Economical process based on simple equipment 3. Easy morphology control ▹ Disadvantages 1. Long reaction time 2. Relatively high defect level
	Ultrasonic chemical synthesis	▸ Advantages 1. Process of normal temperature and pressure 2. Economical process based on simple equipment 3. Short reaction time and high yield ▹ Disadvantages 1. No report about on-substrate of ID ZnO nanostructures 2. Lack of investigation on chemical or physical phenomena

Table. 1 summarizes the types and characteristics of ZnO nanostructure synthesis. Synthesis methods can be classified into vapor phase synthesis methods and solution phase synthesis methods. The vapor phase synthesis methods which have been generally used from the beginning to the present include chemical vapor phase deposition, metal-organic chemical vapor deposition (MOCVD) and pulsed laser deposition (PLD). The solution phase synthesis methods, which have been actively studied in recent years, are characterized by reaction at low temperatures and includes hydrothermal and sonochemical methods. When sonochemical synthesis is performed in an aqueous solution, a structure is formed on the surface of the sensor due to chemical reactions such as equations (1) to (5). This is because such a nanostructure has a larger surface area than a general bulk structure, thereby making a lot of changes in the resistance value to improve the response characteristics.

$$(CH_2)_6N_4 + 6H_2O \rightarrow 4NH_4 + 6HCHO \quad (1)$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \quad (2)$$

$$Zn + 4NH_4^+ \rightarrow Zn^{2+} + 2NH_3 + H_2 \quad (3)$$

$$Zn^{2+} + 4OH^- \rightarrow Zn(OH)_4^{2-} \quad (4)$$

$$Zn(OH)_4^{2-} \rightarrow ZnO \quad (5)$$

Table- II: Key Factors of Sonochemical Deposition Process

Parameter	Characteristics
Frequency	As frequency increases, the time of expansion cycle decreases and the cavitation effect of ultrasonic chemical synthesis increases
Solvent viscosity	As the solvent viscosity increases, the cavitation threshold increases
Solvent surface tension	Cavitation threshold increases due to an increase in surface energy per unit area of solvent
Solvent vapor pressure	As the vapor pressure of the solvent increases, it reduces the cavitation threshold and the energy of the cavitation collapse
Bubbled gas	As the amount of bubble gas in the liquid increases, the cavitation threshold decreases
External pressure	The increase in external pressure affects the cavitation threshold, the strength of the cavitation collapse and the sonochemical synthesis
Temperature	As the temperature increases, the cavitation threshold and the energy of the cavitation collapse decrease
Intensity	As the intensity increases, the effect of sonochemical synthesis increases

Table- II summarizes the process factors affecting the sonochemical synthesis. Factors include frequency, solvent viscosity, solvent surface tension, solvent vapor pressure, bubbled gas, external pressure, temperature, and strength. The most influential one is the frequency of ultrasonic waves. In this study, we analyzed changes in nanostructures formed according to the intensity of this frequency, solvent viscosity, and temperature.

B. The fabrication of sensors

In the manufacturing procedure, since it is not bonded to the Zinc seed layer on the Al_2O_3 substrate, the platinum was coated by an ion coater. The thickness of Platinum was about 80 Å as the bonding layer. The Zn membrane with 1000 Å thickness was vacuum-metallized by the sputtering equipment using a metallic Zinc as the seed layer. To make ZnO, substrates were heat-treated at 600 °C for 1 hour in the furnace. The substrates were treated with a dissolving solution of the zinc nitrate hexhydrate[$Zn(NO_3)_2 \cdot 6H_2O$] and hexamethylene tetramine [$C_6H_{12}N_4$] in de-ionized water. The whole process is as shown in figure 1. If stirring is not carried out, various ZnO-structures are not created. To help the ZnO-structures, the solution is stirred for 15 minutes or more by the stirrer. And the sonochemical deposition was carried out for 1 hour to fabricate a ZnO nanostructure sensor.

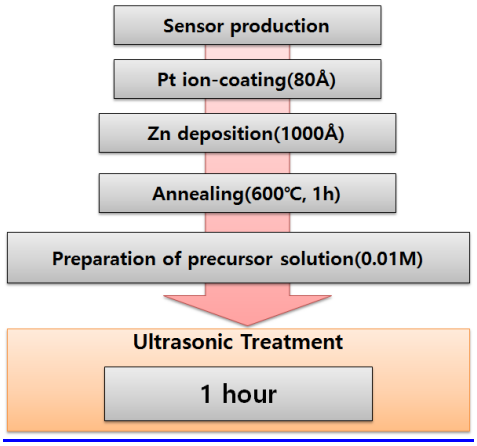

Fig. 2. The manufacturing process for the semiconductor type gas sensor (Figure 2)

By using the ultrasonic radiation (500W, 20KHz), the ultrasonic was applied for the condition time in the designated surface area. Using the ultrasonic process, the Zinc thin film on the substrate was transformed to the form of ZnO-structure by the cavitation effects as shown in figure 3. Because of the cavitation effects, the formation and collapse of the ZnO-structure are achieved. In addition, the ultrasonic chemical deposition has various parameters such as the applied power, temperature and time. In the case of the sonochemical deposition the experiment was carried out under the optimum conditions shown in the previous studies although there are various parameters. Since it is an explosion in the aqueous solution, it affects only the local region of the substrate so that a strong chemical reaction can be applied at a low temperature as a whole.

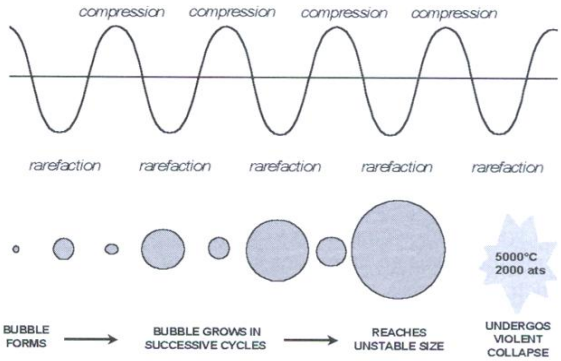

Fig. 3. Growth mechanism of the sonochemical deposition method(Figure 3)

For the fabrication of ZnO semiconductor gas sensor, the equipment and reagents were used as shown in figure 4. 200 ml of D.I. water zinc nitrate hexhydrate [Zn (NO3) 2 · 6H2O] and hexamethylene tetramine [C6H12N4] were prepared at a ratio of 0.01M, respectively.

The previous studies showed that the sensitivity of the sensor was lowered when the concentration of the aqueous solution was high or low. And if it is not sufficiently stirred, the desired structure will not be formed, so it should be stirred for more than 15 minutes using a stirrer. And an ultrasonic sonicator is used to deposit the structure on the sensor surface for 1 hour. The reason is that when the deposition time is short, the structure is formed into a less structured particle shape, and when the time is longer, the structure is broken and the structure is not formed properly. Finally, heat treatment was performed at 600 ° C for 1 hour to improve the mechanical and chemical physical properties of the metal. This process led to the fabrication of nanostructured sensors using ZnO.

Fig. 4. Equipment and reagents used in the fabrication of sensors(Figure 4)

III. REVIEW CRITERIA SENSOR PERFORMANCE EVALUATION

A. The fabrication of sensor's substrate

To experiment sensor's sensitivity on input and output, sensing circuits are manufactured. The power is designed with 5V sensor and heater parts, respectively. Load resister of 68 kΩ is used to larger voltage because currents are small as shown in the figure 5. If the amplified resistance is not used, the resistance of the sensor is so small that the voltage does not change.

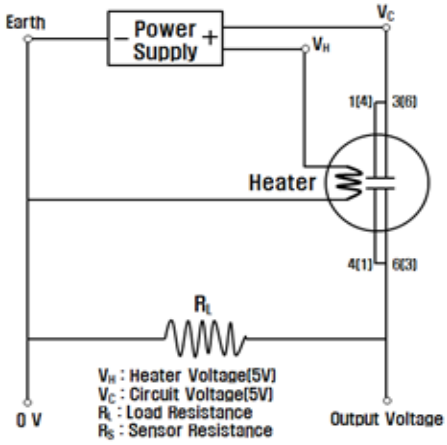

Fig. 5. A sensing circuit for a semiconductor gas sensor (Figure 5)

B. The test equipment of sensors for sensitivity

To test sensor's performance, equipment such as a power supplier, an oscilloscope, a sensing circuit PCB and standard gases are prepared as shown in the figure 6. The power is supplied with 5V sensor and heater parts respectively for keeping surface temperature of a sensor. While standard gases are injected, instantly changeable voltages are measured on an oscilloscope screen. First, basic voltages are measured without injecting gases. Six standard gases are manufactured from 15% LEL CH_4 to 40% LEL CH_4.

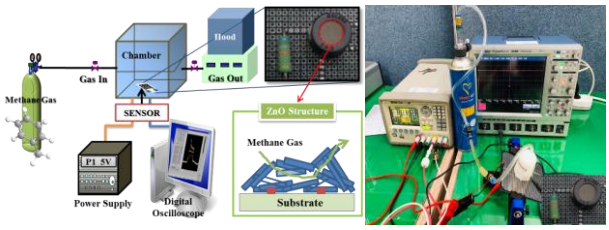

Fig. 6. The test equipment of sensors for sensitivity(Figure 6)

C. Sensors made by sonochemical method

In Figure 7, FE-SEM was used to check if the nano structure is deposited on the surface of the fabricated sensor. 20,000 times and 50,000 times magnified images were taken, and the thickness and length of the nano-structure were measured and displayed in 50,000-time pictures. A portion of the surface of the sensor was taken, and it was found that the nanostructure was uniformly deposited. The thickness of ZnO nanostructures was 70 ~ 90nm and the length was 600 ~ 1300nm. In the previous study, it was found that the ZnO thickness and length could be manipulated according to the concentrations of the aqueous solution, and the optimization of the concentration of the aqueous solution was applied to this study. The formation of such a nanostructure will greatly contribute to increasing the sensitivity of the sensor by increasing the surface area that reacts with gas on the sensor surface. In addition, increasing the surface area could contribute to the production of high-sensitivity micro-sensors.

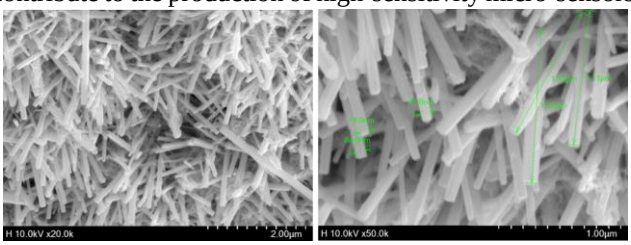

Fig. 7. The FE-SEM analysis of ZnO nano-structure(Figure 7)

The XRD analysis was carried out to find out whether ZnO is deposited on the fabricated sensor. The peak value of the material is displayed graphically above each peak value. The square, the triangle and circle represent Al_2O_3, Platinum and ZnO, respectively. The XRD plot in Figure 8 shows the peak values for all three materials (ZnO, Platinum, Al2O3). First, Al_2O_3 is a material used as the substrate of the sensor, Platinum was used as the adhesive material to help the deposition of ZnO, and ZnO was deposited on the surface of the sensor in the form of a nano-structure.

This shows that the ZnO nano-structure was deposited on the surface of the sensor.

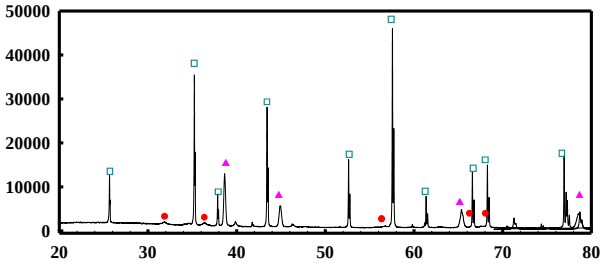

Fig. 8.The XRD analysis of ZnO nano-structure(Figure 8)

D. Evaluation of ZnO Sensor Durability

A sensing test was conducted for 1 year to evaluate the durability of the sensor. It was tested by fixing to a gas of Methane 45 % LEL concentration. A total of 12 tests were conducted once a month for a year. Although the sensitivity value did not show a big deviation, the sensitivity of the sensor changed slightly due to the influence of temperature and humidity. As shown in Figure 9, it was found that the sensitivity of the sensor was maintained constantly for one year, and it was judged that it could be used as a sensor.

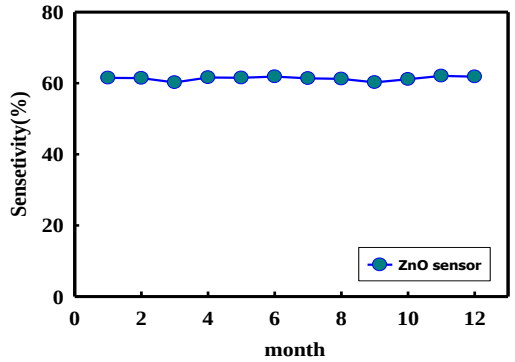

Fig. 9. Evaluation of sensor's long-term durability(Figure 9)

E. Sensor performance test

For methane gas, certified standard gas was used and a total of 6 concentrations were used. To test the sensor's performance, we flowed methane gas to test if it reacts within less than 1 second and checked if it reacts continuously for 10 seconds. We also checked if it recovers rapidly within less than 10 seconds and returns to the state of initial voltage value when methane gas is cut off. Table 3 summarizes the test results. The manufactured ZnO sensor passed the three sensor performance tests and was judged to have suitable performance as a sensor. The average of the voltage values collected for 10 seconds, the voltage value before sending methane standard gas and the difference between the two voltage values were expressed as average voltage, basic voltage and difference, respectively.

Table- III: The value of the average voltage and basic voltage

Methane gas [LEL(%)]	Average Voltage(V)	Basic Voltage(V)	Differences(V)
15	4.851	3.826	1.025
20	4.878	3.831	1.047
25	4.885	3.835	1.050
30	4.891	3.826	1.065
35	4.905	3.821	1.084
40	4.909	3.82	1.089

As shown in Table 3, test results are generated. After that, active voltages are measured with injecting Methane standard gases by 6 types of concentration. Average voltage is 4.851V when injecting 15% LEL CH_4, basic voltage is 3.862V. The difference of voltages is 1.025V. Average voltage is 4.909V when injecting 40% LEL CH_4, basic voltage is 3.82V. The difference of voltages is 1.089V. This experiment showed that the higher the concentration of methane standard gas, the higher the voltage value. We are to complement it through linear regression analysis because less complete linearity may lead to poor utility as a detector.

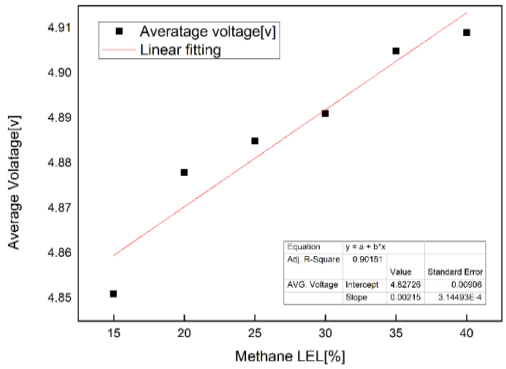

Fig. 10. The sensitivity of Sensor by Methane Gas Concentration (Average Voltage)(Figure 10)

In Figure 10, the values of the equations obtained through linear regression analysis are shown as red lines. The linear regression analysis graph used the following expressions (6) ~ (8) to derive the equation. The derived graph showed linearity, making it possible to expect that it will increase the utilization as a detector.

$$Y = mX + c \tag{6}$$

$$nc = m\sum_{i=1}^{n} X_i = \sum_{i=1}^{n} Y_i, \qquad c\sum_{i=1}^{n} X_i^2 = \sum_{i=1}^{n} X_i Y_i \tag{7}$$

$$m = \frac{n\sum_{i=1}^{n} XiYi - \sum_{i=1}^{n} Xi \sum_{i=1}^{n} Yi}{n\sum_{i=1}^{n} X_i^2 - (\sum_{i=1}^{n} Xi)2}, \qquad c = \frac{\sum_{i=1}^{n} Yi \sum_{i=1}^{n} X_i^2 - \sum_{i=1}^{n} Xi \sum_{i=1}^{n} XiYi}{n\sum_{i=1}^{n} X_i^2 - (\sum_{i=1}^{n} Xi)2} \tag{8}$$

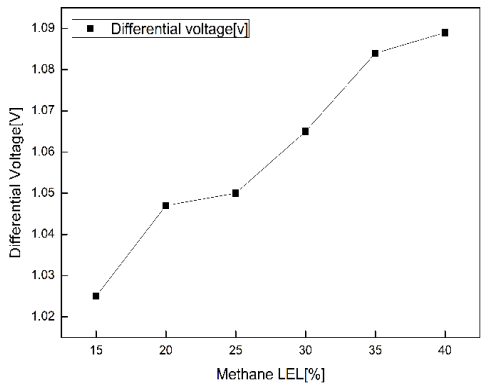

Fig. 11. The sensitivity of Sensor by Methane Gas Concentration (Based Voltage)(Figure 11)

Figure 11 shows the graph using the data on difference of voltage values. It can be seen that there is not much difference between the voltage values in the methane 20 ~ 25% section and 35 ~ 40% concentrations. Since this may cause problems in measuring the exact concentration of methane gas, we are to improve the process method of the sensor to improve this. We want to make the linear shape of the graph by changing the structure using the variables of the sonochemical deposition method. In order to secure more data in the future, we will experiment using methane standard gas concentrations from 0 to 100% LEL.

IV. RESULT AND DISCUSSION

We manufactured a highly sensitive oxide semiconductor type methane gas sensor with a simple process. And We measured the change of the voltage before and after the Methane gas injections to judge whether it had a suitable performance as the Methane gas sensors. Through various experiments, it was confirmed that the proper performance was achieved as a sensor.

1) A nanostructured sensor was fabricated using sonochemical deposition.
2) The sensor was exposed to gas for one year and showed good properties in long-term durability.
3) Good linearity was shown through experiments by standard gas concentration.

V. CONCLUSIONS

We developed a semiconductor that the thin films of Pt and Zn were coated with on the electrode. Thin films of Pt are fabricated by ion plasma and Zinc is manufactured by DC sputtering methods. Then the deposited boards were produced by ultrasonic process in 0.01 M aqueous solution of $C_6H_{12}N_4$ (Hexa-Methylene Tetramine) and $Zn(NO_3)_2 \cdot 6H_2O$ (Zinc Nitrate Hexa-hydrate). We made the ZnO, prepared samples heat-treated at 600 °C for 1 hour and measured the sensitivity of ZnO-structured sensors for Methane gas. In the experiment, the concentrations of Methane gas ranged from 15% to 40% LEL CH_4. We verified the change of the voltage before and after injections of the Methane gas. It can be judged whether it had a suitable performance as the Methane gas sensors. As a result of the sensitivity of the fabricated sensor, it was found that the voltage increases according to the injection of increased concentration of Methane. The sensitivity of the sensor constantly increased, so the graph showed a linear shape. Also, the fabricated sensors showed very short stabilization time, fast reaction and recovery. As a result, the using possibility of the detector is suggested where detection is required.

ACKNOWLEDGMENT

This research was supported by the Ministry of Trade Industry and Energy under the theme of "Feasibility study of multi energy Hub based on Intelligent Energy Platform(20193510100010)"

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