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Analysis on Response Characteristics of Semiconductor Methane Gas Sensor 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 0.01M aqueous solution of $C_6H_{12}N_4$ and $Zn(NO_3)_2{\cdot}6H_2O$. To make the Zinc oxide, prepared-substrates were annealed at 600℃ for 1h and analysis on response characteristics of ZnO-structured sensors are tested for Methane gas. In the experiments, the concentration of Methane gas was used from 15% to 40% LEL. We measured the change of the voltage before and after the Methane gas injections, it was judged whether it had a suitable performance as the Methane gas sensors. As a result of the sensitivity of the fabricated sensor, it was confirmed that the voltage increases according to the Methane concentration. The sensitivity of the sensor was constantly increase so the graph showed a linear shape. Also, the fabricated sensors showed a very short stabilization time, fast reaction and recovery. As a result, the using possibility of the detector is suggested in the industrial facilities.

Keywords- *Heat-treatment, ZnO-structure,Methane, Ultrasonic process*

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I. INTRODUCTION

Methane, CH4, is a colorless, odorless gas with a wide distribution in nation. Methane gas is a hydrocarbon-based gas composed of carbon and hydrogen, which 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 (100% LEL) or higher. Therefore, this gas may cause a large fire of damage to human life, so it is always necessary manage it [1].

In the last decades, Zinc-Oxide 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. Zinc-oxide-based materials are used in gas sensors because of their numerous benefits, such as good response characteristics and so on [2].

The sensing method of the semiconductor gas sensor for the target gases by using a high temperature (300~400℃) and the surface properties change because of the conductivity of the electron exchange of gas when gas is absorbed on the surface of Zinc oxide semiconductor. Zinc-Oxide 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. So as to adsorb as much of the Methane gas as possible on the sensor's surface area, giving a stronger and more measurable response characteristics [4].

In this paper, we developed Methane gas sensor that can be used for the Methane gas detector installed in the plant. To manufacture the toxic gas sensor, first of all, Al_2O_3 substrates which were Ion-coated with the Pt and Zn film was deposited for the Zinc seed layer on each side were prepared. Pt and Zn film were fabricated by ion plasma and DC sputtering deposition equipment, respectively. In addition to turn the deposited zinc powder into zinc oxide, the gas sensors were heat-treated at 600 ℃ for one hour. Then gas sensors of ZnO-structure were manufactured by ultrasonic process in an aqueous solution of 0.01M.

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

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II. Experimental Method

A. *The fabrication of sensor's substrate*

The size of sensor's substrate is 4.5mm ×3.78mm×0.3t. It consists of gold electrodes and an Al_2O_3 substrate. The resistance of platinum heater (back side) is approximately 15 ohm. To prevent short circuits, the electrodes have positioned the holes in the semiconductor Methane gas sensors.

B. *The manufacturing process*

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 80Å as the bonding layer. The Zn membrane with 1000Å thickness was vacuum-metallized by the sputtering equipment using a metallic Zinc as the seed layer. To make Zinc oxide, substrates were heat-treated at 600℃ during the 1hour by the furnace. The substrates were treated with a dissolving solution of the zinc nitrate hexhydrate[Zn(NO3)2·6H2O] and hexamethylene tetramine [C6H12N4] in de-ionized water. Whole process is like figure 1. If stirring is not carried out, various ZnO structures are not created. To help the ZnO-structures, solution is stirred for 15 minutes or more by the stirrer.

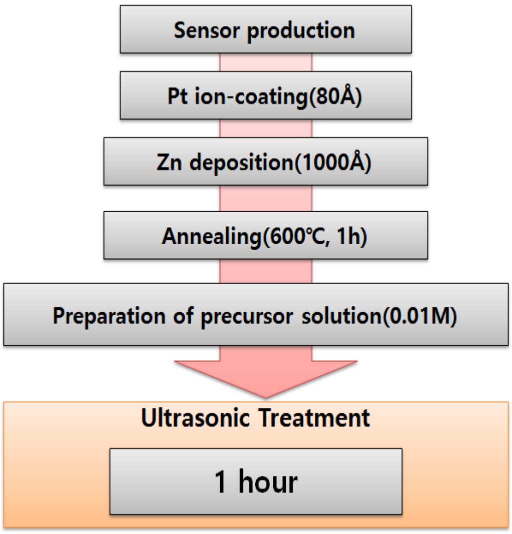

Figure 1. The manufacturing process for the semiconductor type gas sensor

C. *The ultrasonic chemical deposition*

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 2. Because of the cavitation effects, the formation and collapse of the ZnO structure are achieved. In addition, the ultrasonic chemical vapor deposition has various parameters such as the applied power, temperature and time. In the case of the ultrasonic process the experiment was carried out under the optimum conditions shown in the previous studies although there are the 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 low temperature as a whole.

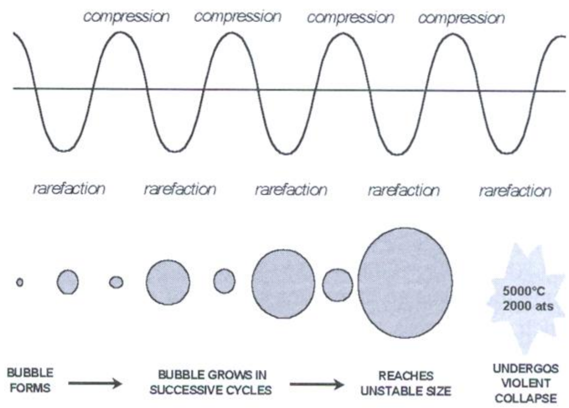

Figure 2. Growth mechanism of the ultrasonic method

For the fabrication of ZnO semiconductor gas sensor, the equipment and reagents were used in figure 3. After 0.01M reagent is added in 200ml distilled water, they are stirred in a stirrer for 15minutes. If an aqueous solution is enough stirred, the ultrasonic chemical deposition cannot be occur, so a stir is needed for long time relatively.

Figure 3. Equipment and reagents used in the fabrication of sensors

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III. Design of the Test System

A. *The production of sensor's circuit*

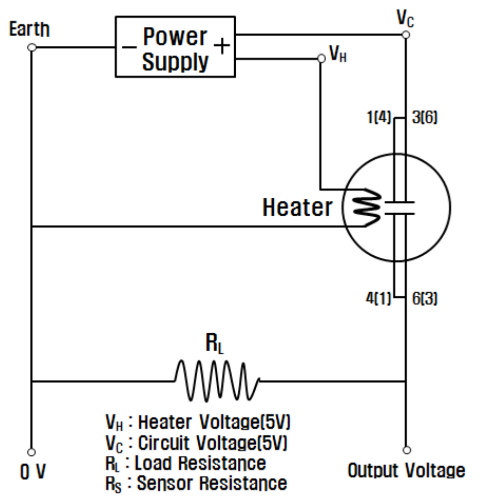

Figure 4. A sensing circuit for a semiconductor gas sensor

To experiment sensor's response characteristics on input and output, sensing circuits are manufactured. The power is designed with 5V sensor and heater parts respectively. Load resister is used of 68k kΩ to larger voltage because of current is small as shown in the figure 4. If the amplified resistance was not used, the resistance of the sensor is a very small that the voltage does not change.

Design of circuits for measuring gas sensors

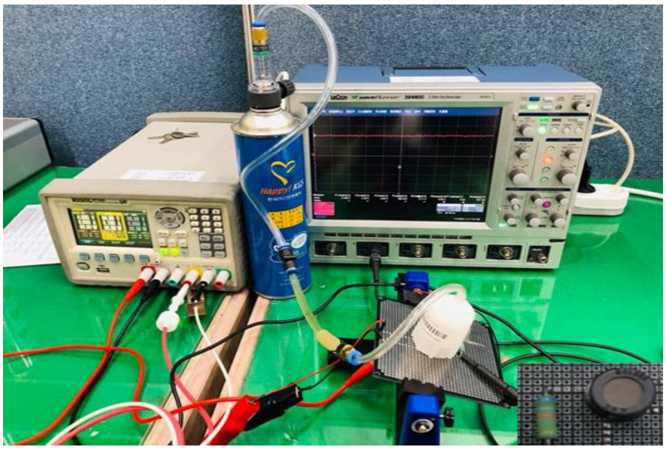

Figure 5. The test equipment of sensors for response characteristic

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 5. f. 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 CH4 to 40% LEL CH4.

IV. Experiments and Results

TABLE 1. THE VALUE OF THE AVERAGE VOLTAGE AND BASED VOLTAGE

Standard gases [LEL(%)]	Average Voltages(V)	Basic Voltages(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 shwon in Table 1, test results are generated. Above all, basic voltages are measured without standard gases. After that, active voltages are measured with injecting standard gases by 6 type concentration. Average voltage is 4.851V when injecting 15% LEL CH4, basic voltage is 3.862V. The difference of voltages is 1.025V. Average voltage is 4.909V when injecting 40% LEL CH4, basic voltage is 3.82V. The difference of voltages is 1.089V. We verified output voltages are continuously increasing against injecting standard gases. Figure 6 shows graph of response characteristic induced by least square method of linear regressions. The equation to represent relations of input and output is a little error, the field of gas safety can be used. Also, the differences of the measured voltages are verified from figure 7.

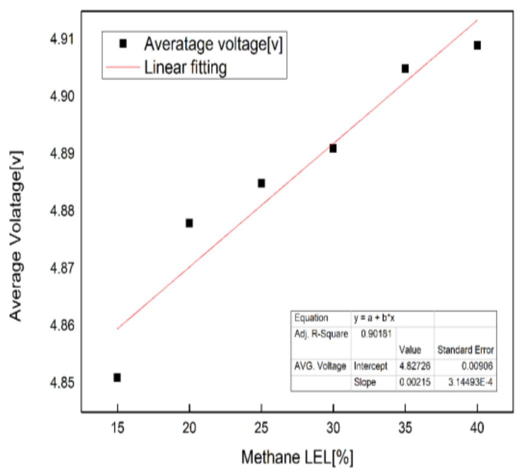

Fig. 6 The response Characteristics of Sensor by Methane Gas Concentration (Average Voltage)

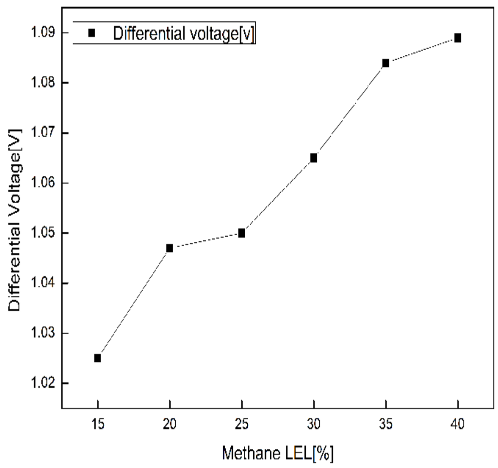

Figure 7. The response Characteristics of Sensor by Methane Gas Concentration (Based Voltage)

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 0.01M 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 Zinc oxide, prepared samples heat-treated at 600℃ for 1h, and analysed response characteristics of ZnO-structured sensors for Methane gases. In the experiments, the concentration of Methane gas was used from 15% to 40% LEL CH4. 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 confirmed that the voltage increases according to the injection of increased concentration of Methane. The sensitivity of the sensor was constantly increase so the graph showed a linear shape. Also, the fabricated sensors showed a very short stabilization time, fast reaction and recovery. As a result, the using possibility of the detector is suggested in the industrial facilities.

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