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Methane Gas Sensing Properties of the Zinc Oxide Nanowhisker-derived Gas Sensor

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A low power methane gas sensor with microheater was fabricated by silicon bulk micromachining technology. In order to heat up the sensing layer to operating temperature, a platinum (Pt) micro heater was embedded in the gas sensor. The line width and gap of the microheater was 20 μm and 4.5 μm, respectively. Zinc oxide (ZnO) nanowhisker arrays were grown on a sensor from a ZnO seed layer using a hydrothermal method. A 200 ml aqueous solution of 0.1 mol zinc nitrate hexahydrate, 0.1 mol hexamethylenetetramine, and 0.02 mol polyethylenimine was used for growing ZnO nanowhiskers. Temperature distribution of the sensor was analyzed by infrared thermal camera. The optimum temperature for highest sensitivity was found to be 250℃ although relatively high (64%) sensitivity was obtained even at as low a temperature as 150℃. The power consumption was 72 mW at 250℃, and only 25 mW at 150℃.

Keywords: Gas sensor, Microheater, Zinc oxide, Nanowhiskers, Methane

1. INTRODUCTION

Recent research show, methane to be a gas that affects global warming 20 times more severely than carbon dioxide. It is explosive, due to its high volatility and flammability in air [1]; and in closed areas, methane gas may cause suffocation. Therefore development of a reliable and economical methane gas sensor is needed. Micro gas sensors using CMOS or CMOS-MEMS technology are being developed and applied because of their small size, light weight, low power, fast response, suitability to mass production, and low production cost [2,3].

Oxide semiconductor gas sensors have high sensitivity and a fast response speed compared with other sensors. They are easy to manufacture, and the addition of appropriate catalysts allows the sensors to be selective to specific gases [4-7]. Their operation is mainly based on the change of conductivity of an oxide surface caused by adsorption and desorption, which occurs when the reactive gas is exposed to sensing film. In order to measure gas sensitivity, the temperature of the sensing material should be maintained at over 300℃ uniformly through the gas adsorption and desorption processes [8]. A heater is necessary for this reason; this results in a massive power consumption problem [9].

To reduce the power and increase the sensitivity of the gas sensor, nanotechnology-derived nano-sized gas sensing membranes have been developed. The detection method of a semiconductor-based gas sensor is based on surface reaction. Since nanomaterial-based sensors have a large detection surface area, they have relatively higher sensitivity and lower power consumption compared to bulk sensors [10-12]. ZnO can be synthesized into nanotube, nanowire or nanorod forms, depending on synthesis technique and post-processing. By applying different catalysts, they may exhibit selectivity for certain types of gas.

We have developed a gas sensor for methane gas sensing using bulk micromachining technologies, utilizing a ZnO nanowhisker-derived sensing layer and a platinum (Pt) micro-heater. Using the pulsed laser deposition (PLD) method, a ZnO seedlayer was

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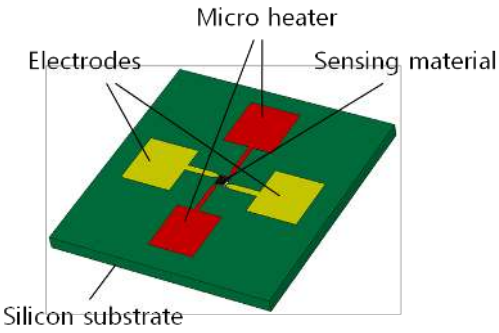

Fig. 1. Schematic diagram of the gas sensor structure.

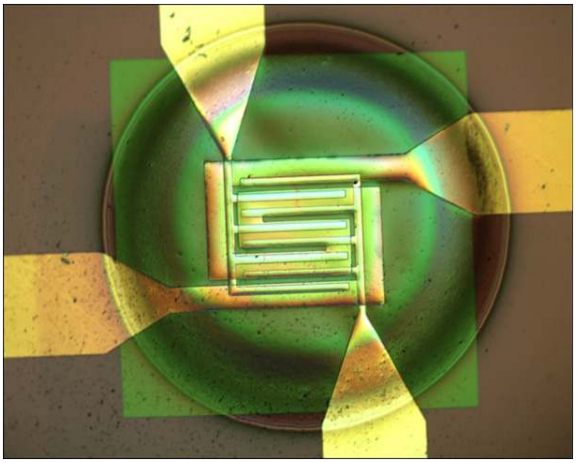

Fig. 2. Optical image of fabricated sensor.

deposited and ZnO nano-whiskers were hydrothermally synthesized from the ZnO seed layer. To enhance the sensing property of methane gas, palladium (Pd) and silver (Ag) were deposited on the ZnO nanowhisker using an e-beam evaporator.

2. SENSOR FABRICATION

Figure 1 shows a schematic diagram of the proposed gas sensor. A p-type (100) double-side polished silicon wafer with resistivity of 6 Ω·cm and thickness of 495 μm was used as a substrate. Low stress nitride with a thickness of 1,600 Å was then deposited on the substrate using a low pressure chemical vapor deposition (LPCVD) method. To define a wet etching mask, silicon nitride was etched using reactive ion etcher (RIE). For a diaphragm structure, the back of the substrate was etched with 30 wt% potassium hydroxide (KOH). The microheater and sensing electrode were defined using photolithography. Titanium (Ti) and platinum (Pt) materials were deposited and annealed to use as a microheater. Their thickness was 200 Å and 2,000 Å, respectively. To insulate the microheater and sensing electrode, silicon dioxide with a thickness of 4,000 Å was deposited using a plasma enhanced chemical vapor deposition (PECVD) method. After deposition of a passivation layer, a gold (Au) electrode was patterned using photolithography and an e-beam evaporator.

A ZnO seed layer of 1,000 Å was deposited on the membrane's active layer by a pulsed laser deposition (PLD) method, as shown in Fig 2. Figure 3 shows the x-ray diffraction curves of ZnO seed layer deposited on the silicon substrate. The dominant peak observed at 2 θ = 34.4° was (002)-oriented ZnO, and the full

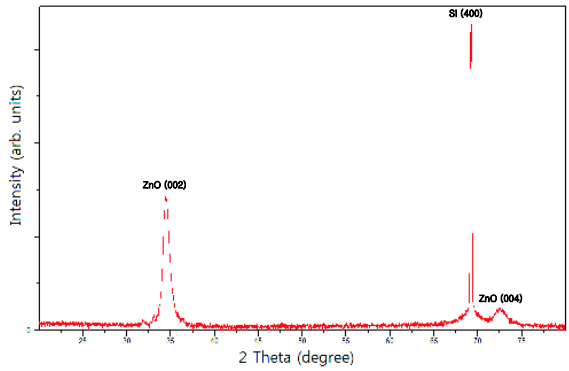

Fig. 3. XRD pattern of the ZnO seed layer deposited on the silicon substrate.

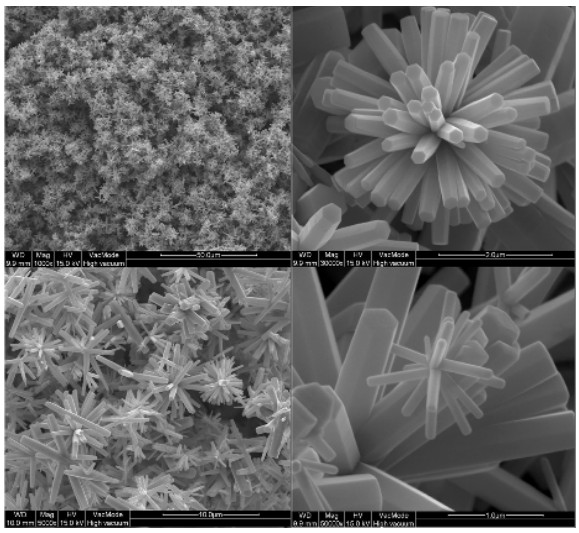

Fig. 4. SEM images of hydrothermally grown ZnO nanowhiskers arrays.

width at half maximum (FWHM) of the peak was 0.4488. ZnO nanowhisker was synthesized from the deposited ZnO seed layer using the hydrothermal method. The sensor was then dipped into a solution containing 0.1 mol zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), 0.1 mol hexamethylene tetramine ($C_6H_{12}N_4$) and polyethylenimine ($(C_2H_5N)_n$) and heated on a hot plate. The temperature was set to 90℃, and the total time of synthesis was 24 hours. A temperature sensor was used to measure temperature during synthesis, and the temperature range was 90 ± 1.5℃. The sensor was then cleaned with ethanol and DI water and dried for 24 hours in a 90℃ oven. To enhance the methane gas sensing property, Pd and Ag materials were evaporated for the thickness of 20 Å using co-deposition. After drying, the sensor was produced in a 600℃ nitrogen atmosphere for 30 minutes each. The ZnO nanowhisker grown by the proposed method was analyzed by SEM image, and shown in Fig. 4.

3. RESULTS AND DISCUSSION

3.1 Microheater heating and power consumption properties

To measure the energy required for the microheater to reach the operating temperature, the operating voltage was varied with

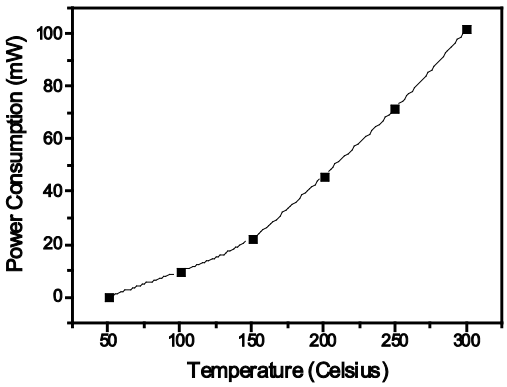

Fig. 5. Power Consumption of microheater with temperature.

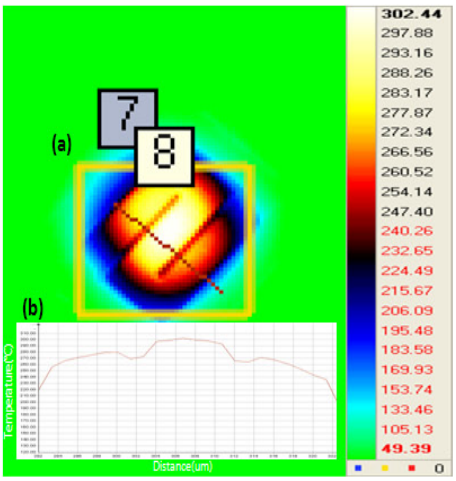

Fig. 6. Temperature profile of microheater at 2.2 V.

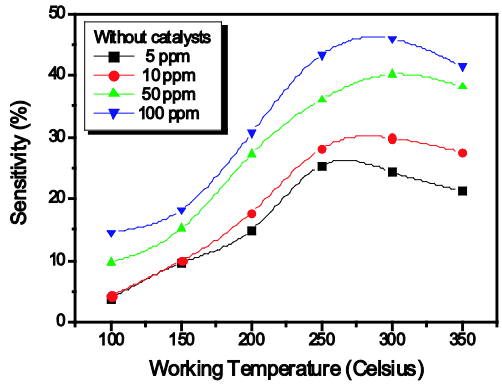

Fig. 7. Sensitivity of the ZnO nanoshisker sensor without catalysts as a function of temperature for various methane concentrations.

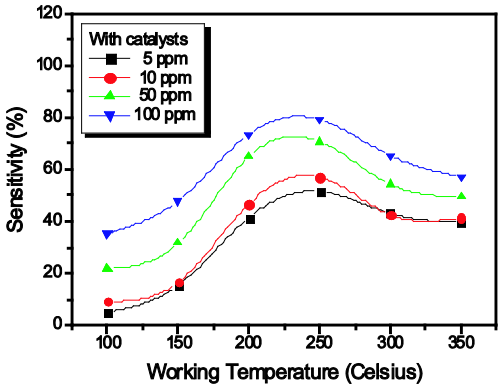

Fig. 8. Sensitivity of the ZnO nanowhisker sensor with Pd and Ag catalysts as a function of temperature for various methane concentrations.

temperature up to 300℃. Figure 5 shows the power consumption of the microheater in different temperatures. The Pt microheater had a power consumption of 102 mW and thermal efficiency of 2.94℃/mW at 300℃ temperature. Figure 5 shows the temperature profile of the microheater when a 2.2 V operating voltage is applied. The picture was taken using an infrared thermo. Figure 6(a) shows that most of the heat is concentrated near the origin of heating because of the membrane's superior insulation quality. Figure 6(b) graphically displays the temperature profile of the microheater where the heat dissipates from the center of the heater to the outer diaphragm. The center of the heater reached a maximum temperature of 302℃ and the outer-most boundaries reached a minimum temperature of 220℃. The conformation of the heater was a strip line that had a line width of 20 μm and line gap of 4.5 μm. The temperature difference between the lines was 30℃ at maximum and the average temperature of the microheater was about 260℃. An operating voltage of 2.2 V showed a 5% error rate under conditions of 250℃.

3.2 Methane gas sensing properties

The ZnO nanowhisker-based gas sensor was tested for its sensing property of methane gas in different concentrations (5, 10, 50, 100 ppm) and in different temperatures (from 100℃ to 300℃ by increments of 50℃). Sensitivity was measured by injecting the gas into atmospheric air. As in Equation (1), the difference between sensor resistivity in air (R_a) and sensor resistivity during gas reaction (R_g) was calculated against the resistivity in air.

$$S = \frac{(R_a - R_g)}{R_a} \times 100[\%] \quad (1)$$

Figures 7 and 8 show the operating temperatures of the ZnO nanowhisker sensor and the (Pd, Ag)-evaporated catalysis sensor against the sensing property for different methane concentrations. ZnO nanowhisker sensor, sensitivity appeared to increase as the operating temperature and the methane concentration increased. In relatively high temperatures (> 200℃) and high concentrations (> 50 ppm), the sensitivity was about 30~45%. For the ZnO nanowhisker sensor with catalysts (Pd, Ag), sensitivity increased as the operating temperature and gas concentration increased. In relatively high temperatures (> 200℃) and high concentrations (> 50 ppm), the sensitivity was about 50~80%. However, in operating temperature over 300℃, sensitivity was reduced (~15%). Such phenomenon can be explained by the results from Yamazoe's research. The speed of adhesion to and detachment of methane gas from oxide semiconductor surfaces increases as the temperature increases, until it reaches a specific temperature point where the rate reaches its maximum. The optimal sensitivity and sensing rate depends on the rate of adhesion to and detachment of gas molecules from the surfaces of the sensor [13].

The sensitivity of the catalysts (Pd, Ag) sensor was 1.8-fold higher than that of the ZnO nanowhisker sensor. According to Kohl's research, methane gas separates into methyl group and hydrogen as a result of hydrogen bonding at the membrane

surface, and the bonded hydrogen atoms create a hydrogen molecule.

$$CH_{4gas} \leftrightarrow CH_{3ads} + H_{ads} \quad (2)$$

$$H_{ads} + H_{ads} \rightarrow H_2 \quad (3)$$

Hydrogen molecules react with oxygen on the Pd, Ag surface to produce H_2O. This organic radical goes through a series of chain reactions to finally produce CO_2. Metals, such as Pd and Ag, act as catalysts in oxidizing flammable gases, such as methane, which greatly increase the rate of reaction [7,13]. Sensitivity increased as concentration increased; however, from 5 ppm to 10 ppm, only about a 3% average increase was shown, whereas higher concentrations yielded a higher increase rate (17%, 30%). The operating temperature of 250℃ was found to be the optimal temperature for all concentrations of gas. For concentrations higher than 100 ppm, the relatively low operating temperature of 150℃, yielded a sensitivity of 64%, which is about 81% of the optimal temperature value (79% @250℃). The power consumption under 150℃ and 250℃ operating temperatures was 25 mW and 72 mW, respectively. An operating temperature of 150℃ only used a third of the power required for an operating temperature of 250℃.

4. CONCLUSION

The MEMS process was used to produce a 2.6 mm × 2.6 mm sensor with 20 μm heater lines and 4.5 μm gaps on a membrane of 800 μm × 800 μm surface area as a strip line form. A gas sensor with internalized Pt microheater was evaporated from a ZnO seedlayer using PLD, and ZnO nanowhisker was developed by hydrothermal synthesis as the sensing material. To enhance the sensing property of methane gas, Pd and Ag were used as catalysts, and the sensing property was confirmed by exposing the sensor to different concentrations of methane gas under different operating temperatures. As a result of the measurement, an operation temperature of 250℃ was found to be optimal under all concentrations of gas. When the methane gas concentration was 100 ppm and the operating temperature was 250℃, the sensitivity was found to be 79% and the power consumption was 72 mW. When the operating temperature was 150℃, the power consumption was 25 mW and the sensitivity was 64%. This result indicated that a 150℃ operating temperature consumed only a third of the power of the maximum sensitivity condition, but still showed superb sensitivity.

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