Hybrid gas sensor having TiO$_2$ nanotube arrays and SnO$_2$ nanoparticles

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Abstract: To obtain a good performance of gas detection, a newly-designed metal oxide semiconductor gas sensor has been fabricated by micromachining process. The micro platform consisted of Pt heater and electrode and its size was 2.5 mm × 2.5 mm. For hybrid sensing materials, such as SnO$_2$ nanoparticles and TiO$_2$ nanotube arrays were deposited on the micro platform. To obtain a clean and open window of TiO$_2$ nanotube, two-step anodic oxidation was conducted. The diameter of window and length of TiO$_2$ nanotubes were ~60 nm and ~5.5 µm, respectively. Detection performances for CO and CH$_4$ gases were investigated with operation circuit at operating temperature of 100°C and 300°C, respectively. The power consumption of fabricated micro platform was 28 mW and 94 mW at 2 V and 4 V of heater voltages, respectively. High sensitivity and short response time were observed. The microstructures of gas sensor were systemically characterised by FESEM and X-ray diffraction patterns.

Keywords: gas sensor; MEMS; platform; hybrid; TiO$_2$ nanotube; SnO$_2$; CO; CH$_4$.

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## 1 Introduction

Recently, there have been many studies on the development of various gas sensors for the enhancement of human convenience and safety. Increasing attention on health hazard caused by pollution has driven the development of gas sensing for real-time environmental monitoring [1]. Metal oxide gas sensors have been widely used in portable gas detection systems owing to many advantages such as high sensitivity, fast response and good reproducibility including long-term stability, and possibly coupled with low cost and portability [2,3]. The chemiresistive semiconducting metal oxide gas sensors are the most practical and effective gas detection method because of their simple structure and operation [4].

However, the power consumption is crucial issue in gas sensor operation for extension of its useful applications, such as mobile equipment. Micro-electro-mechanical system (MEMS) process is attractive fabrication method for gas sensor application. MEMS gas sensor has a various advantages such as a small size device, low power consumption, high and fast sensing response and recovery with low concentration [5]. Generally, MEMS device comprises a thermally isolated thin Si$_3$N$_4$ membrane suspended within a silicon wafer, microheater which controls the operation temperature, insulating layer, interdigitated electrodes, and a sensing materials layer on the top of the platform. The low-stress silicon-nitride based membrane serves to reduce power consumption, down to 5–100 mW with heating to the effective operation temperature for certain gases [6].

Tin dioxide (SnO$_2$) is a typical n-type semiconducting metal oxide and is one of the attractive gas sensing materials because of its wide bandgap, physical stability and wide operation temperature (200–600°C) for various detection gases [7]. SnO$_2$ based
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Sensing materials have been used for the detection of various gases owing to its thermal and chemical stability. Through the chemical modification of SnO\textsubscript{2} based materials and optimisation of operation conditions, high sensitivity, selectivity and response of were achieved [8–11]. Titanium dioxide (TiO\textsubscript{2}) is chemically stable and electrically semiconductive. TiO\textsubscript{2} nanotube arrays have extended the application area to sensing materials including gas sensing and bio-medical materials [12–14]. The TiO\textsubscript{2} and SnO\textsubscript{2} system in field of gas sensing has been extensively studied which shows different electronic features such as band gap energies and work functions. The mixture of both metal oxides with specific ratio could enhance the gas sensing properties and kinetics of the responses [15]. Generally, although metal oxide gas sensors have good performance for certain gases, their operation temperatures are very high which increases their operation power requirement, impede their integration within circuit, and makes them undesirable to be used with flammable gas.

In this work, we have designed and fabricated gas sensor platform including micro heater and sensing electrode using MEMS processes. The size of fabricated gas sensor platform was designed 2.5 mm × 2.5 mm. The hybrid semiconductor metal oxides as a gas sensing materials, TiO\textsubscript{2} nanotube arrays and SnO\textsubscript{2} nano-powder have been mounted on the platform. TiO\textsubscript{2} nanotube arrays were synthesised by two-step anodic oxidation. The gas sensing performances with carbon monoxide (CO) and methane (CH\textsubscript{4}) gases with its power consumptions and operation temperatures were investigated. The microstructures of hybrid sensing materials were systematically characterised by FESEM and X-ray diffraction patterns.

2 Experimental

The platforms for gas sensor were fabricated by MEMS processes. A double side polished p-type Si substrate (100) with 4 inch diameter and 500 µm thickness was prepared for the production of a low stress 2 µm thick SiN\textsubscript{x} film that was deposited using a low pressure chemical vapour deposition process (LPCVD). A patterned platinum (Pt) film was used for the micro-heater to increase the temperature and to better activate the sensing materials. Titanium (Ti) was used for the adhesive layer between the SiN\textsubscript{x} and Pt. The heater layer of Pt on Ti was etched using a dry etching process with advanced oxide etching (AOE) equipment. An insulating layer of SiO\textsubscript{2}/SiN\textsubscript{x}/SiO\textsubscript{2} with a thickness of 1 c was deposited on the patterned heater layer. A sensing electrode layer of Ti/Pt film was deposited using a sputtering process, and was then patterned using a dry etching process. After finishing the front side processes of the wafer, the SiN\textsubscript{x} membrane for the low power consumption gas sensor was created on the back side of the wafer. The 2 µm thickness of SiN\textsubscript{x} on the back side of the wafer was etched by RIE (reactive ionic etching), and window patterned Si wafer was etched in 25 vol.% of KOH solution at 80°C for 8 h with protection of the front side. Then 1.0 mm × 0.8 mm of SiN\textsubscript{x} membrane was created and indicated by a yellow square in Figure 1(b). Finally, gas sensor platform including heater and electrode on the 2 µm thickness of SiN\textsubscript{x} membrane was designed and fabricated as shown in Figure 1.

The chip of platform was designed 2.0 mm × 2.0 mm and membrane on the platform was 0.8 mm × 1.0 mm in size. The micro heater for control of operation temperature was patterned on the membrane and its width was designed 2 µm. The temperature of micro heater was measured by infrared camera (ThermoCAM P25, FLIR system, Sweden)
while various input voltages were applied up to 300°C by DC power source. From these results, power consumptions were investigated with temperature of the platform.

**Figure 1** (a) The structure of gas sensor platform and (b) configuration of fabricated platform (see online version for colours)

TiO$_2$ nanotube array were fabricated by two-step anodic oxidation, and schematic diagram of anodic oxidation system is shown in Figure 2. The system consisted of a power supply, multimeter, constant temperature bath, and computer. The power supply and multimeter were computer-controlled by the LabVIEW program for anodic oxidation. The anodic oxidation was conducted by a potentiostatic method. Titanium foil (0.89 mm thickness, 99.7 % purity, Alfa Aesar, South Korea) was anodised in ethylene glycol electrolyte with 0.5 wt.% NH$_4$F at 60 V for 1 h with 30°C. Then the TiO$_2$ nanotube arrays through the first anodic oxidation were removed by ultra-sonication and dried. The anodic oxidation was conducted with same procedure immediately. The TiO$_2$ nanotube arrays fabricated two-step anodic oxidation were heat treated in a furnace at 400°C for 30 min. The crystalline structure of the annealed TiO$_2$ nanotube arrays was observed by XRD (X-ray diffractometer, Rigaku D/MAX-RC, Cu K$_\alpha$ radiation, Japan). Then, additional anodising was performed at 20 V for 1 h after detachment from Ti metal plate. The detached TiO$_2$ nanotube arrays were transplanted on centre of electrode area of MEMS platform which was printed with SnO$_2$ nanopowder by a scalpel
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Through the heat treatment at 450 °C for 1h, TiO$_2$ and SnO$_2$ hybrid sensing material was mounted on the MEMS platform. The microstructures of the detached TiO$_2$ nanotube arrays and SnO$_2$ hybrid sensing materials were determined by field-emission scanning electron microscopy (FESEM, Philips/Fei XL 30SFEG, Netherlands) at the Korea Basic Science Institute.

Figure 2  Schematic diagram of the anodic oxidation system with the LabVIEW program (see online version for colours)

![Diagram of anodic oxidation system with LabVIEW program](image)

The gas sensing properties of the CO and CH$_4$ gases were tested at 2 V (~100°C) and 4 V (~300°C) of heater voltages, respectively. The gas concentrations of the CO and CH$_4$ were measured: 25, 50, 100, 200, 300 ppm for CO and 500, 1000, 3000, 6000, 12,500, 25,000 ppm for CH$_4$. The gas sensor was operated in the gas measurement chamber which has 8 litre volume, the calculated gas volumes of those concentrations were injected using a gas-tight syringe. Figure 3 shows the simple circuit which was operated a gas sensor in the chamber, measured the voltage across load resistance ($V_{out}$) as a sensing signal.

Figure 3  Schematic diagram of the basic circuit for sensor operation (see online version for colours)

![Simple circuit for sensor operation](image)

$V_{IN}$: Circuit voltage; $R_S$: Sensor resistance; $R_L$: Load resistance; $V_{OUT}$: Voltage across load resistance.
3 Result and discussion

3.1 The power consumption and surface temperature

Figure 4 shows the power consumptions with heater voltage ($V_{H}$) of MEMS platform, and thermal images of platform for 2 V and 4 V of $V_{H}$ are shown in Figure 5(a) and (b), respectively. The average power consumptions of the MEMS platform were typically increased. For detecting CO gas, the power consumption of 28 mW was measured at heater voltage of 2 V. The power consumption of 94 mW was also measured at heater voltage of 4 V for detecting CH₄ gas. The temperatures observed by thermo-graphic camera for CO and CH₄ gases were 98.9°C and 271°C, respectively. To maintain a high detecting performance, CH₄ gas needs the higher temperature of 271°C than 98.9°C for CO gas.

Figure 4 Measurement of power consumptions with heater voltage ($V_{H}$) of the platform
(see online version for colours)

Figure 5 The thermal images of the temperature of platform surface measured by infrared camera (Thermo CAM P25, FLIR system, Sweden) with heater voltages ($V_{H}$), (a) 2 V and (b) 4 V (see online version for colours)

(a) (b)
3.2 Characterisation of sensing materials

To fabricate the gas sensor, sensing materials were prepared using the hybrid sensing materials TiO$_2$ nanotube array on the SnO$_2$ nanopowder. Figure 6 shows the X-ray patterns of the annealed TiO$_2$ nanotube arrays after second anodic oxidation. The peaks of the anatase structure of the TiO$_2$ and Ti metal were observed. The peak of the Ti metal resulted from the Ti substrate. The TiO$_2$ anatase structure was transformed from amorphous as-anodised nanotube arrays.

![Figure 6](image)

Figure 6 The X-ray patterns of the annealed TiO$_2$ nanotube arrays after second anodic oxidation (see online version for colours)

Figure 7 shows FESEM images of the hybrid sensing materials composed of TiO$_2$ nanotube arrays and SnO$_2$ nanoparticles mounted on MEMS platform. Figure 7(a) and (b) are the top view and cross-sectional view of the hybrid sensing materials. There were hexagonal marks on the surface of the TiO$_2$ nanotube arrays and they were the traces of the TiO$_2$ nanotube arrays obtained from first anodic oxidation. The TiO$_2$ nanotube arrays fabricated by the second anodic oxidation had the clean and open windows. The diameter of the window and the length of the TiO$_2$ nanotubes were 60 nm and ~10 µm, respectively. The thickness of SnO$_2$ nanoparticle layers was ~4 µm and the layer acted as sensing and adhesive materials.

3.3 Sensing properties to CO and CH$_4$

Figure 8 shows the detecting performance of the hybrid gas sensor with CO and CH$_4$ gases. The output voltage (\(V_{\text{out}}\)) means a voltage across load resistance and the values were measured at load resistance of 850 kΩ. The resistance of sensor was decreased owing to CO and CH$_4$ gases adsorption to the hybrid sensing materials. The voltage across load resistance (\(V_{\text{out}}\)) was finally increased. For CO gas, as shown in Figure 8(a), the difference of \(V_{\text{out}}\) between air and gases with CO gas concentration was increased.
The values measured at heater voltage of 2 V were 61 mV for 25 ppm, 125 mV for 50 ppm, 218 mV for 100 ppm, 349 mV for 200 ppm, and 462 mV for 300 ppm. The difference of $V_{\text{out}}$ between air and gases with CH$_4$ gas concentration was also increased in Figure 8(b). The values measured at heater voltage of 4 V were 413 mV for 500 ppm, 526 mV for 1000 ppm, 906 mV for 3000 ppm, 1094 mV for 6000 ppm, 1301 mV for 12,500 ppm, and 1462 mV for 25,000 ppm. The results were summarised in Table 1. The results reveals that the variation range of output voltage level for CO and CH$_4$ gases show 1.0~1.5 V for CO and 2.5~4.0 V for CH$_4$ at different operation temperatures and the gas selectivity of CO and CH$_4$ could be enhanced by changing the operation temperature.

**Figure 7** FESEM images of the TiO$_2$ nanotube arrays: (a) top view and (b) cross-section view
**Figure 8** Output signals of gas response for (a) CO with 2 V of $V_H$ input and (b) CH$_4$ with 4 V of $V_H$ input as a function of gas concentrations (see online version for colours)

**Table 1** Summarised sensitivities of fabricated micro-gas sensors to CO and CH$_4$

<table>
<thead>
<tr>
<th>Gas</th>
<th>Concentration (ppm)</th>
<th>$V_{out}$ (mV)</th>
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<tbody>
<tr>
<td>CO</td>
<td>25</td>
<td>61</td>
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<tr>
<td></td>
<td>50</td>
<td>125</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>218</td>
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<tr>
<td></td>
<td>200</td>
<td>349</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>462</td>
</tr>
<tr>
<td>CH$_4$</td>
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<tr>
<td></td>
<td>1000</td>
<td>526</td>
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<td>6000</td>
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<td></td>
<td>12,500</td>
<td>1301</td>
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<td></td>
<td>25,000</td>
<td>1462</td>
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</table>
4 Conclusion

The hybrid gas sensors were fabricated using MEMS processes and have a good thermal stability and durability during the experiments. The power consumption of platforms was 28 mW and 94 mW at effective operation temperatures of CO and CH₄ gases, respectively. The hybrid sensing materials were TiO₂ nanotube array prepared by two-step anodic oxidation on SnO₂ nanopowder. Gas detection performances were investigated in range of 10~300 ppm CO gas and 500~25,000 ppm CH₄ gas, and the sensitivities ($\Delta V_{out}$) of 61~462 mV for CO and 413~1462 mV for CH₄ were observed. The range of out voltage shows the split-level, 1.0~1.5 V for CO and 2.5~4.0 V for CH₄, for two kinds of gases. It will be possible to detect CO and CH₄ selectively.

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References

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