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LETTER

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Methane and hydrogen sensing properties of catalytic combustion type single-chip micro gas sensors with two different Pt film thicknesses for heaters

Woongjin Jang[1,2], Joon-Shik Park[1*], Ki-Won Lee[3] and Yonghan Roh[2]

Abstract

A catalytic combustible type single-chip micro gas sensor was fabricated by MEMS technology and responses with input powers and methane and hydrogen gas concentrations were characterized. The ranges of responses at Pt thickness of 450 nm and input power of 128 mW were 1.076–2.433 mV for methane concentrations of 2315–5787 ppm, and 0.965–2.514 mV for hydrogen concentrations of 282–706 ppm, respectively. The ranges of responses at Pt thickness of 150 nm and input power of 112 mW were 0.192–0.438 mV for methane concentrations of 2315–5787 ppm and 0.949 mV to 2.496 ppm for hydrogen concentrations of 282–706 ppm, respectively. The responses to H_2 concentration ratios were 3.65 mV/10^3 ppm for a micro gas sensor with a 450 nm thick heater and 3.81 mV/10^3 ppm for a micro gas sensor with a 150 nm thick heater. But in the case of methane gas response, the response to concentration ratios of the micro gas sensor using the 150 nm thick Pt heater was remarkably different from the case of the 450 nm thick Pt heater. The ratios for CH_4 were 3.51 mV/10^4 ppm for the micro gas sensor with a 450 nm thick heater and 0.6 mV/10^4 ppm for the micro gas sensor with a 150 nm thick heater, respectively. From these results, the micro gas sensor that has the thicker heater with a thickness of 450 nm showed higher sensitivity to methane gas than the micro gas sensor with a thinner heater with a thickness of 150 nm.

Keywords: Single-chip, Catalytic, Combustible, Micro gas sensor, Methane and hydrogen gases, Pt heater

Background

It is expected that the production of natural gas will inevitably increase for a while until the switch to sustainable and eco-friendly energy sources. Natural gas, a "bridge fuel," is known to have environmental credentials but the benefits are marred by leaks from human activities and natural sources [1–4]. A micro-scale gas sensor will likely be able to quantitatively measure leaks with low power consumption and speediness. And along with quantity, another topic for the micro gas sensor, is recognizing the type of gas. The response of a micro gas sensor might be suitable for a location but it is usually hard to recognize what type of gas it is. The main component of natural gas, methane, is sometimes blended with hydrogen, and there is commercial interest due to the effectiveness and low emissions of NO_x [5]. However, the gas sensing of microchips have limits of selectivity and stability to exceed the current level [6, 7]. A variety of ways of enhancing gas selectivity have been tried. The Cu-BTC metal–organic framework was used as a sensing layer and measured work function [8]. In the field of semiconducting types, working temperature-modulating frequencies, grain size of the sensing layer film, filter use, and the facet properties of the surface of sensing materials have shown potential as methods to obtain selectivity [9–11]. Besides chemical approaches, the refractive index changes of the sensing layers [12] and the resonance frequency of the sensor for gas type [13] have been investigated. The combustible type gas sensor is a transducer that converts the

*Correspondence: jspark@keti.re.kr
[1] Smart Sensor Research Center, Korea Electronics Technology Institute, Seongnam-si, Gyeonggi-do 13509, Republic of Korea
Full list of author information is available at the end of the article

heat of a combustion reaction into an electric signal. The reactivity leads to a response that varies with different gases in the equal condition of intensive property, and a catalytic combustible type gas sensor could be able to harness this variety to discriminate chemicals.

In this work, the micro gas sensor platforms embedding thin film micro-heaters with a meander structure were realized by the MEMS process. The film heater has less power consumption than the coil of the traditional pellistor type by between one order and two orders of magnitude [6]. The catalytic combustible type micro gas sensors were measured and how to discriminate between hydrogen and methane gas was studied.

Methods

Design and fabrication

A sensing device and compensation device were integrated into the single-chip micro gas sensor. Each of the thin film layers of the micro gas sensor was fabricated under same conditions as in previous work [14] except for the design and thickness of the heaters. Here, we briefly describe the fabrication process as follows. Using low pressure chemical vapor deposition (LPCVD), 2 μm thick SiN_x film was deposited on a 500 μm thick, 4-inch double-sided polished p-type Si(100) wafer. And 10 nm Ta/150 nm Pt film was deposited as a micro heater, and patterned using the reactive ion etching (RIE) process on the front side of the wafer. Using the plasma-enhanced chemical vapor deposition (PECVD) method, a $SiO_x/SiN_x/SiO_x$ layer was deposited as an insulator layer, and then patterned for the formation of an electrode pad using the RIE process. The backside of bulk silicon was anisotropically etched to form membranes in KOH solution after patterning the SiNx film using the RIE process. The thicknesses of the heater that were deposited were 150 nm and 450 nm due to a trade-off between power consumption and response or output voltage. The micro platform for the single-chip micro gas sensor, which consists of a sensing device and compensation device, was fabricated with a size of 5.9 mm × 3.9 mm. The sensing device and the compensation device were connected in a series and the electrodes of the micro gas sensors were one output and two input. In order to have same resistance, the micro patterns of both devices were defined with symmetry. Shinwoo Electronics Co., Ltd. provided the sensing materials to use for the micro gas sensors. The fabricated micro platforms were mounted on TO-8 using epoxy and the electrode pads were bonded to packages with gold wires. The average resistance for the 450 nm thick heaters was 41.2 Ω and the average for the 150 nm thick heaters was 292.3 Ω. After applying sensing materials paste to the heater of the sensing device, the paste was dried to evaporate the organic solvent at 200 °C for 15 min. The structure of the micro platform and image of the micro gas sensor can be seen in Fig. 1.

Temperature characteristics of the micro heaters using two different Pt film thicknesses

The temperatures of the Pt heaters with electric input power were measured with an IR camera (MobIR M8, Wuhan Guide Infrared Co., Ltd.). The emissivity of the object was set for 0.2 [15]. The measurement was carried out for one heater of the two heaters in single chip before the application of the catalyst materials, and the results are shown in Fig. 2.

Gas sensing measurement

The gas sensing performances of the fabricated micro gas sensors were studied with the following steps. The micro gas sensor package was connected to the socket of a 1728 cc static acrylic container. The socket was connected to a Wheatstone bridge circuit outside the container by cable. As for gases for the test, 10% methane was balanced with argon and 1.22% hydrogen was balanced with nitrogen. After electric power was supplied, in operation mode, the output voltage was regulated to nearly 0 V and a certain amount of gas extracted from the cylinder was injected into the container. It was assumed that the injected gases were most immediately diffused throughout the container, and uniform concentrations were made. The micro gas sensor responded to the gas and the output voltage was reached within 25 s in all cases. After 1 min, the mixed gas of air and test gas was released outside by a rotary pump connected to the container. Fresh air was replaced through an inlet at the same time, and then the output voltage recovered to the initial value. When the signal levelled off, the measuring steps were repeated. The output voltage values were automatically recorded every 5 s using a multi-meter (Model: Fluke 287) and PC.

Results and discussion

The ranges of responses or output voltages of micro gas sensors with a 450 nm thick heater were from 1.076 to 2.433 mV for methane concentrations from 2315 to 5787 ppm (Fig. 3a), and 0.965–2.514 mV for hydrogen concentrations of 282–706 ppm (Fig. 3b). The micro gas sensors with 150 nm thick heaters, the responses were 0.192–0.438 mV for methane concentrations of 2315–5787 ppm (Fig. 3c) and 0.949–2.496 ppm for hydrogen concentrations of 282–706 ppm (Fig. 3d). The micro gas sensor with two 450 nm thick heaters consumed power of 128 mW and the micro gas sensor with two 150 nm thick heaters consumed 112 mW, respectively. The input powers with Pt heater thicknesses and responses or output

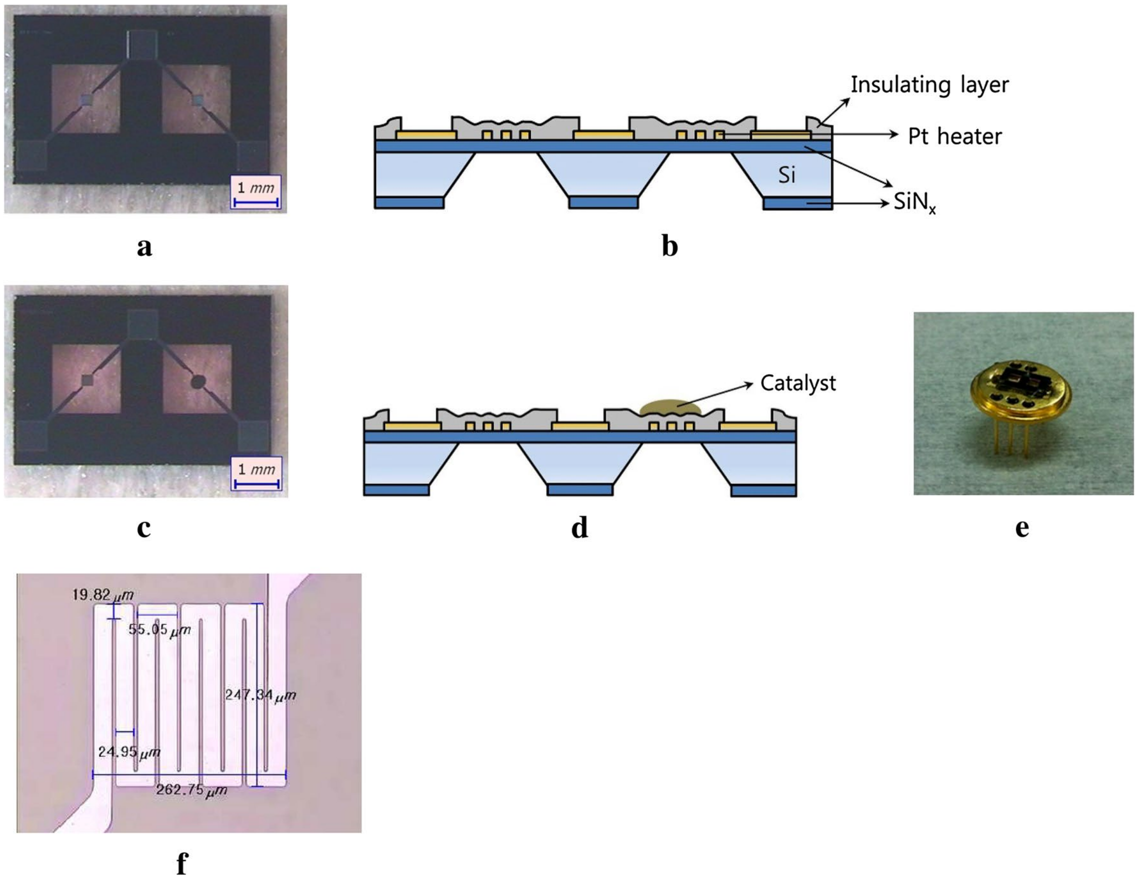

Fig. 1 Images of the catalytic combustible type single-chip micro gas sensor platforms: top view of fabricated micro gas sensor platforms without catalyst materials (**a**) and with catalyst materials only on the right-hand side membrane (**c**). **b**, **d** Schematic views of the cross-section structures of **a** and **c**. **e** Image of single-chip micro gas sensor platform **c** packaged on TO-8. **f** Top image of fabricated Pt micro heater in single-chip micro gas sensor platform

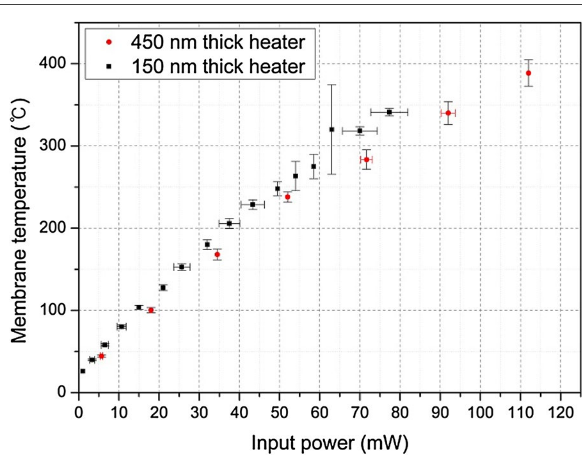

Fig. 2 Graph of input power vs. membrane temperature for one of two heaters in single chip. Two chips were fabricated with 150 nm (square) and 450 nm (circle) thick Pt films for heaters, respectively. So, he total power of two heaters in a single chip is two times the input power indicated in the graph

voltages of catalytic combustible type single-chip micro gas sensors are summarized in Table 1.

The two kinds of Pt thin film micro heaters were designed with the same pattern and two different Pt thicknesses of 150 nm and 450 nm. The electrical input power of the micro gas sensor with a 450 nm thick Pt heater was 128 mW, and the electrical input power of the micro gas sensor with a 150 nm thick Pt heater was 112 mW. Even though the concentration ranges were different between hydrogen gas in the several hundreds and methane gas in the several thousands, in the case of hydrogen gas response, the response to concentration ratios of the micro gas sensor using a 150 nm thick Pt heater was quite similar to the case of 450 nm thick. The response to H_2 concentration ratios were 3.65 mV/103 ppm for the micro gas sensor with a 450 nm thick heater and 3.81 mV/10^3 ppm for the micro gas sensor with a 150 nm thick heater, as shown in Fig. 4. But, in the case of methane gas

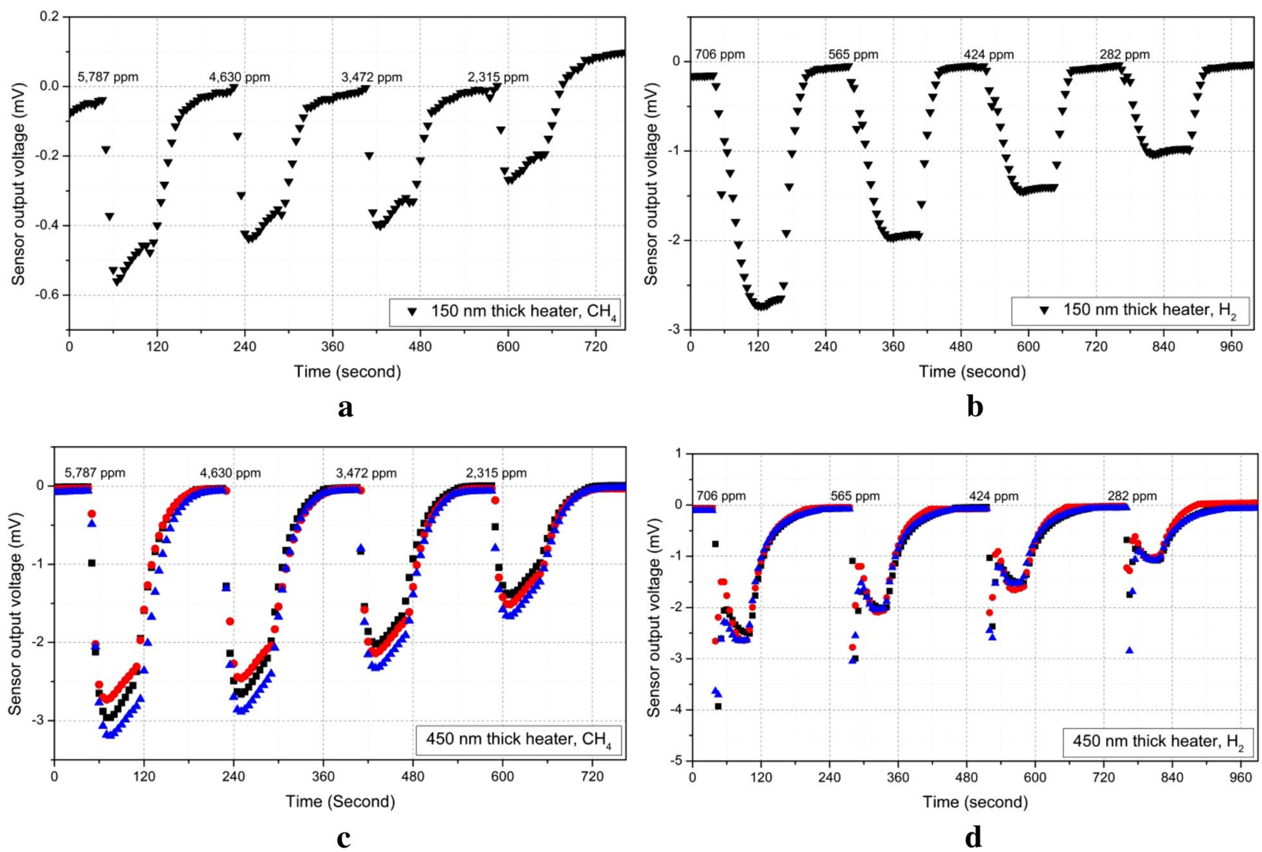

Fig. 3 Gas response properties of catalytic combustible type single-chip micro gas sensors to varying concentrations of CH_4 and H_2 gases: **a**, **b** one micro gas sensor with 150 nm thick heater, **c**, **d** three micro gas sensors with 450 nm thick heaters

Table 1 Responses to methane and hydrogen gas concentrations of fabricated catalytic combustible type single-chip micro gas sensors with two different Pt heater thicknesses and input powers

Input		Output			
Pt heater thickness (nm)	Input power (mW)	CH_4 concentration response		H_2 concentration response	
		ppm	mV	ppm	mV
150	112	2315	0.192	282	0.949
		3472	0.326	424	1.350
		4630	0.367	565	1.900
		5787	0.438	706	2.496
450	128	2315	1.076	282	0.965
		3472	1.719	424	1.480
		4630	2.164	565	1.959
		5787	2.433	706	2.514

response, the response to concentration ratios of the micro gas sensor using a 150 nm thick Pt heater was remarkably different from the case of the 450 nm thick Pt heater. The ratios for CH_4 were 3.51 mV/10^4 ppm for the micro gas sensor with a 450 nm thick heater and 0.6 mV/10^4 ppm for the micro gas sensor with a 150 nm thick heater, as shown in Fig. 4. The responses to the concentration ratios above were obtained through the linear fitting of graphs in Fig. 4 using Origin software from OriginLab®. From these results, the micro gas sensor that had the thicker heater with a thickness of 450 nm showed higher sensitivity to methane gas than the micro gas sensor with the thinner heater with a thickness of 150 nm. It is thought that the 150 nm thick heater at 112 mW provided sufficient energy for hydrogen gas sensing. But, in the case of methane gas sensing, not the 150 nm thick heater but 450 nm thick heaters were required to detect methane gas. Because the thicker Pt heater has a relatively higher temperature coefficient of resistance [16] than the thinner Pt heater, the thicker Pt heater could supply much heat energy to combust methane gas with higher activation energy than the case of hydrogen gas. However, the micro gas sensor with the thinner Pt heater has an economic advantage for hydrogen gas sensing in this work.

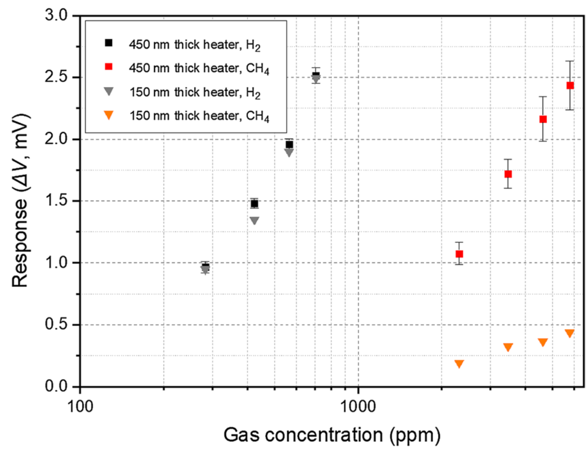

Fig. 4 Response vs. gas concentration of the fabricated catalytic combustible type single-chip micro gas sensors

Conclusions

Catalytic combustible type single-chip micro gas sensors were designed and fabricated with two different heater thicknesses of 150 nm and 450 nm, and responses to methane and hydrogen gases were measured. The responses to H_2 concentration ratios were quite similar, such as 3.65 mV/103 ppm for the micro gas sensor with a 450 nm thick heater and 3.81 mV/10^3 ppm for the micro gas sensor with a 150 nm thick heater. Meanwhile, the responses to CH_4 concentration ratios were remarkably different between 3.51 mV/10^4 ppm for micro gas sensors with 450 nm thick heaters and 0.6 mV/10^4 ppm for the micro gas sensor with the 150 nm thick heater, respectively. From these results, it was seen that the micro gas sensor with the thicker heater with a thickness of 450 nm showed higher sensitivity to methane gas than the micro gas sensor with a thinner heater with a thickness of 150 nm. The catalytic combustible type single-chip micro gas sensor that was developed could be used for the leakage detection of methane and hydrogen gases after a long-term reliability test.

Authors' contributions

WJ and JSP made substantial contributions to conception, fabrication, acquisition of data, and analysis. WJ and JSP were involved in drafting the manuscript and revising it critically for important intellectual content. KWL and YR gave approval for the version. All authors read and approved the final manuscript.

Author details

[1] Smart Sensor Research Center, Korea Electronics Technology Institute, Seongnam-si, Gyeonggi-do 13509, Republic of Korea. [2] Department of Electronic and Electrical Engineering, Sungkyunkwan University, Suwon-si, Gyeonggi-do 16419, Republic of Korea. [3] Shinwoo Electronics Co., Ltd, Hwaseong-si, Gyeonggi-do 18529, Republic of Korea.

Competing interests

The authors declare that they have no competing interests.

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