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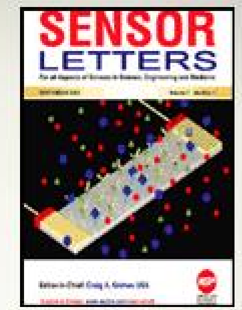
A Micro-Electromechanical System Based Hydrogen Gas Sensor

Authors: Lee, E.B.; Yeo, C.H.; Shin, K.; Lee, K.J.; Lee, H.J.; Lee, W.B.; Ju, B.K.
Source: Sensor Letters, Volume 6, Number 6, December 2008 , pp. 1014-1018(5)
Publisher: American Scientific Publishers



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Abstract:

We describe the fabrication processes and the characterizations of a MEMS (Micro-electromechanical systems) based hydrogen gas sensor. The gas sensor is made by MEMS based on a semiconductor fabrication method except for the ceramic bulk. The heating electrode and sensing electrode were formed being apart from the substrate by using MEMS and SnO_2 ceramic bulk as a gas sensitive material was formed extending over the heating and sensing electrode. The SnO_2 gas sensor with the micro-hotplate showed good response to the H_2 gas at 50–20,000 ppm and high selectivity as compared to other gases as CO, H_2S, and CH_4. The value obtained of the TCR is 1.61×10^{-3} K^{-1}. The TCR of the micro hotplate is lower than the TCR of bulk Pt as the thickness of the micro hotplate is only 2 μm.

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Keywords: MEMS; HYDROGEN; SNO2; TEMPERATURE COEFFICIENT OF RESISTANCE
Document Type: Research article
DOI: 10.1166/sl.2008.552

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SENSOR LETTERS
Vol. 6, 1014–1018, 2008

RESEARCH ARTICLE

A Micro-Electromechanical System Based Hydrogen Gas Sensor

E. B. Lee[1], C. H. Yeo[1], K. Shin[1], K. J. Lee[2], H. J. Lee[3], W. B. Lee[3], and B. K. Ju[1,*]

[1] *Display and Nanosystem Laboratory, College of Engineering, Korea University, Anam-Dong, Seongbuk-Gu, Seoul 136-713, Republic of Korea*
[2] *Korea Basic Science Institute, Korea University, Seoul 136-701, Republic of Korea*
[3] *Seju Engineering, 611-11, Guam-Dong, Yusung-Gu, Daejeon, 305-801, Republic of Korea*

(Received: 23 November 2007. Accepted: 31 July 2008)

We describe the fabrication processes and the characterizations of a MEMS (Micro-electromechanical systems) based hydrogen gas sensor. The gas sensor is made by MEMS based on a semiconductor fabrication method except for the ceramic bulk. The heating electrode and sensing electrode were formed being apart from the substrate by using MEMS and SnO_2 ceramic bulk as a gas sensitive material was formed extending over the heating and sensing electrode. The SnO_2 gas sensor with the micro-hotplate showed good response to the H_2 gas at 50~20,000 ppm and high selectivity as compared to other gases as CO, H_2S, and CH_4. The value obtained of the TCR is 1.61×10^{-3} K^{-1}. The TCR of the micro hotplate is lower than the TCR of bulk Pt as the thickness of the micro hotplate is only 2 μm.

Keywords: MEMS, Hydrogen, SnO_2, Temperature Coefficient of Resistance.

1. INTRODUCTION

In recent years, research for a clean fuel has been progressing rapidly and vigorously. The desired fuel should have zero emissions, be abundant in nature, and efficient. H_2 as a fuel meets all the requirements perfectly. Not only is H_2 readily available in nature but also when combustion takes place the byproducts given out are water and O_2 making it a very environmentally friendly fuel.

Also H_2 dissipates very easily so in the case of a leak it can be considered safer than many heavier gases as it spreads around fast and dissipates. The amount of energy produced by H_2, per unit weight of fuel, is about three times the energy contained in an equal weight of gasoline and nearly seven times that of coal.[1]

H_2 generation has the potential of being cost effective and coupled with the fact that it is renewable makes it an attractive choice as fuel in a variety of applications. Fuel cells, designed based on H_2, are considered to be "batteries of the future." H_2 has a Lower Explosive Limit (LEL) of 4%[2] in air, which means an accumulation of 4% concentration in air is dangerous as even a small spark can ignite the mixture. As H_2 is proposed to be used as the next generation's fuel, this fact of it turning explosive in the event of a leak has to be kept in mind

Hydrogen leak-detection sensors must detect over the general level of ambient H_2 in a variety of environments. These sensors must be able to differentiate between ambient low-level sources of H_2 and undesirable levels generated by a H_2 leak. Containment of H_2 is very difficult, since it diffuses through most materials.[3]

In the last few years, the above mentioned difficulties have led to new developments in silsicon technology. MEMS based gas sensors are small in size. In addition, microelectronics-based processing allows the formation of arrays on one substrate.

This technology shows great promise for overcoming the difficulties of screen-printed ceramic sensors. In this way, the power consumption can be kept very low, with typical values on the order of 30–150 mW, with the substrate remaining almost at ambient temperature.[4–8] This type of thermally heated device, commonly called a micro-hotplate, is used in different applications.[9–12]

In this paper we describe the fabrication processes and the gas characterization of a MEMS based hydrogen gas sensor. The gas sensor is made by MEMS based on a semiconductor fabrication method except for the ceramic bulk. Thus, the volumes of the heating electrode, the sensing

*Corresponding author; E-mail: bkju@korea.ac.kr

1546-198X/2008/6/1014/005 doi:10.1166/sl.2008.552

electrode, and the ceramic bulk are extremely small for use in the gas sensor. The heating electrode, the sensing electrode and the ceramic bulk are located apart from the silicon substrate so that heat capacity and the loss are small. Moreover, because of using the SnO_2 ceramic bulk as a gas sensitive material in the gas sensor, the detection and the physical properties are superior to those of other gas sensors which utilize a thin film ceramic. In addition, gas sensor has an advantage that only two masks are needed for patterning the window and the metal pattern. Furthermore, the mass productivity of batch process type, which is a merit of the semiconductor fabrication method, is still a target of more inventiveness aimed at lowering the manufacturing cost even more.

2. EXPERIMENTAL DETAILS

2.1. Fabrication of Hydrogen Gas Sensor

Two mask processes were used to fabricate the hydrogen gas sensors with the main steps shown in Figure 1. The initial substrate was a 4 inch silicon wafer, double-sided polished, and ⟨100⟩ oriented. Before processing, the substrates were subjected to a standard cleaning process, which removed any organic contaminants, adsorbed layers, and particulates. A standard cleaning process was used before each thin film deposition to ensure adequate adhesion.

1. A 2 μm SiO_2 film, as an insulating layer, was thermally grown on both sides of a silicon substrate with a crystal orientation of ⟨100⟩ at 1100 °C.
2. The insulating layer was patterned by photolithography using mask No. 1. A center portion of one insulating layer formed on one side of the silicon substrate was patterning locally to obtain a window and to become exposed through the window.
3. Mask No. 2 was used for patterning of the heating electrode, sensing electrode, and metal pads. The Cr (20 nm)/Pt (5000 nm) electrodes were subsequently deposited by electron beam evaporation and achieved by a lift-off process. The heating electrode and the sensing electrode were connected to metal pads on top of the insulating layer, respectively. The metal pads on the insulating layer electrically were isolated from the silicon substrate and connected to outer power or a circuit. The metal pattern, including the metal pads, and heating and sensing electrodes were formed in a unit body. That is, the metal pads and heating electrode were formed in a unit body, while the sensing electrode and the other metal pads were formed in a unit body.
4. The silicon substrate was dipped in a KOH solution at 80 °C for 2 hours and the portion of the silicon substrate exposed through the window was patterned by an etching process. The insulating layer and the metal pattern were not etched in the KOH solution so that a cavity with a depth of 150 μm was formed on the silicon substrate.

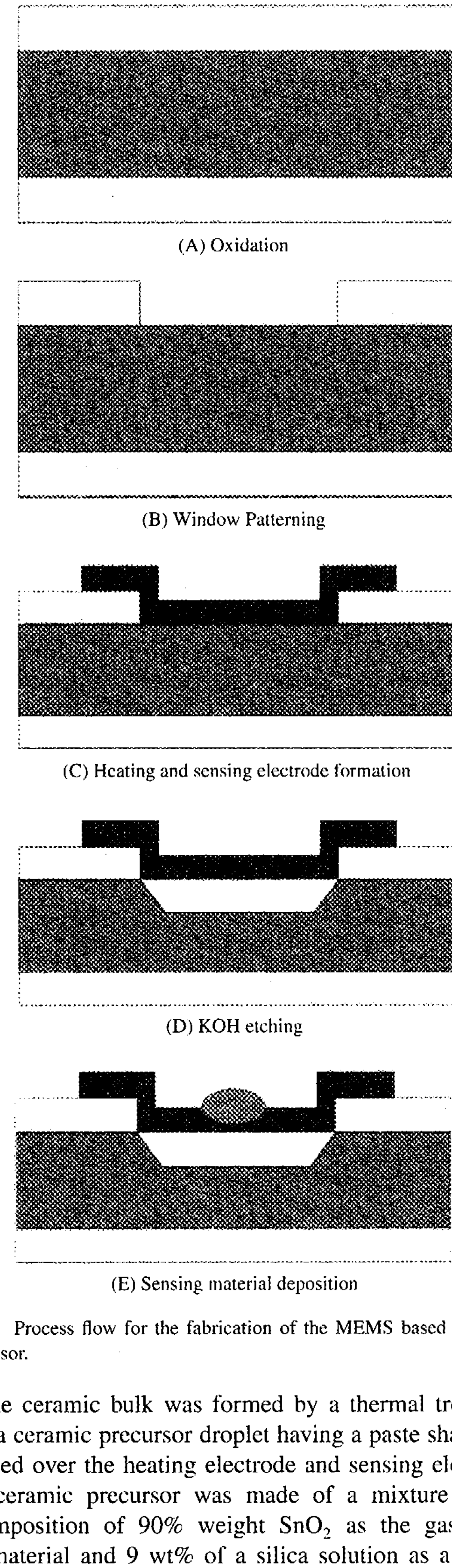

Fig. 1. Process flow for the fabrication of the MEMS based hydrogen gas sensor.

5. The ceramic bulk was formed by a thermal treatment after a ceramic precursor droplet having a paste shape was dropped over the heating electrode and sensing electrode. The ceramic precursor was made of a mixture having a composition of 90% weight SnO_2 as the gas sensitive material and 9 wt% of a silica solution as a binder, and 1 wt% of $PdCl_2$ as a catalyst. The precursor, in a plastic shape, was dropped over the heating electrode and the sensing electrode.

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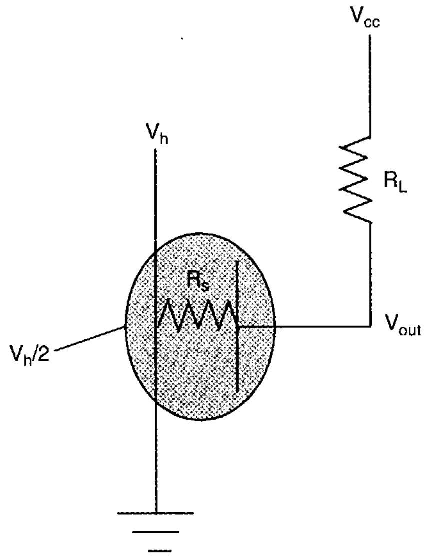

Fig. 2. Measuring electrical circuit of the MEMS based gas sensor.

2.2. Measurement

Gas sensing properties were evaluated in a quartz tube. The sensor device was kept in the middle of a quartz tube (38 mm i.d., 800 mm length). The sensitivity of the gas sensor was measured by a Keithley 2000 multimeter at room temperature. Before the measurement, the gas sensor was maintained for 30 min with an applied voltage in the tube. During the gas response experiment, the output voltage curves of the hydrogen gas sensor were recorded by DAQ, which displayed curves of the voltage versus time. The electric circuit of the measurement of gas response was fabricated as shown in Figure 2. The sensor output V_{out} was expressed by following:

$$V_{out} = R_s \frac{(V_{cc} - V_h/2)}{(R_S + R_L)} + V_h/2 \quad (1)$$

where, V_{cc} is the supply voltage, R_s is the resistance of the sensor, R_L is the resistance of the reference, V_h is the heater voltage, and V_{out} is the measured voltage. Equation (1) can be rewritten as.

$$R_s = R_L \frac{(V_{out} - V_h/2)}{(V_{cc} - V_{out})} \quad (2)$$

3. RESULTS AND DISCUSSION

SEM images of (a) the fabricated microhotplate without sensitive material and (b) the SnO_2 gas sensing material deposited micro dropping onto the suspended micro hotplate were shown Figure 3. The micro hotplate as shown in Figure 3(a) had a dimension of 100 μm × 150 μm. The suspended beams were 10 μm in width. The thickness of the micro hotplate was 2 μm.

The current versus voltage curve of the micro hotplate under steady state is shown in Figure 4. The resistance of the micro hotplate increases with the applied voltage because the data points of the micro hotplate deviate from a straight line. It was reported that the electro-thermal interaction was occurred due to the increase temperature of the active area.[13] This means resistance of the micro hotplate would increase with the applied power.

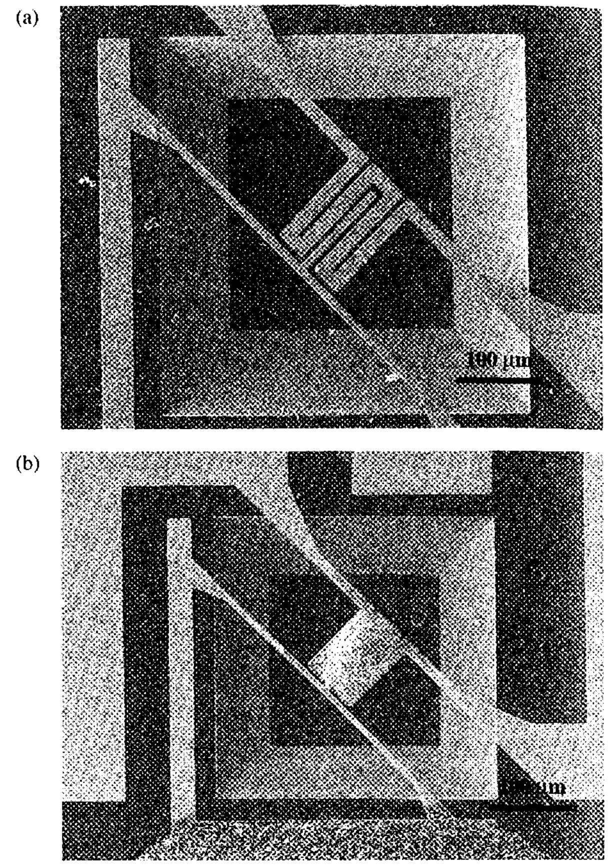

Fig. 3. SEM images of (a) the fabricated microhotplate without sensitive material and (b) the SnO_2 gas sensing material deposited micro dropping onto the suspended micro hotplate.

The temperature properties of the heater and the power consumption of the fabricated micro hotplate have been studied. A micro hotplate was introduced in a precise oven together with a resistive temperature device such as a

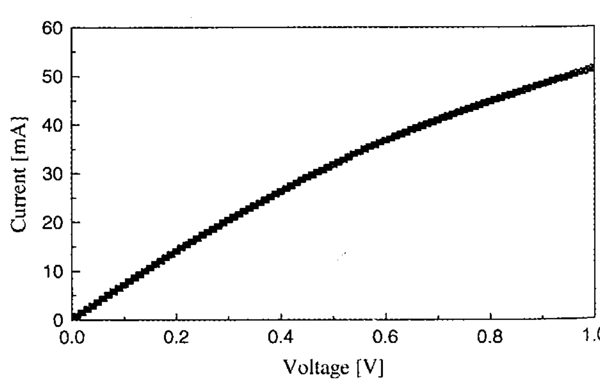

Fig. 4. The current–voltage curve of the micro hotplate.

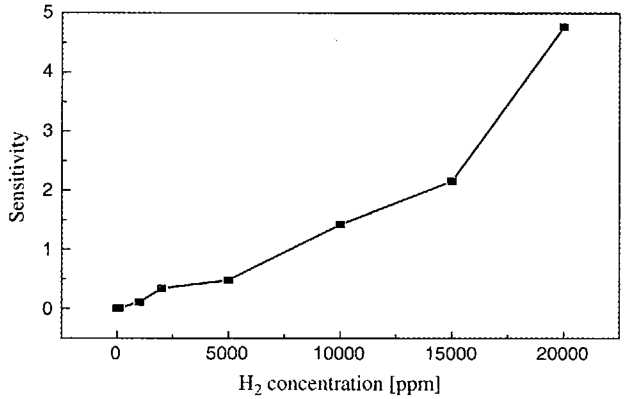

Fig. 5. The sensitivity as a function of H_2 concentration.

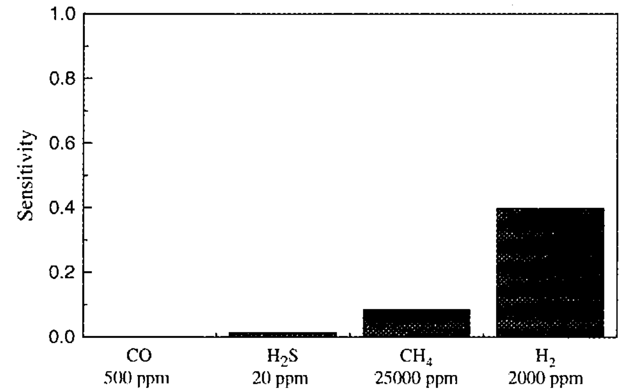

Fig. 6. The sensitivity of the SnO_2 based micro hotplate gas sensor to other gases.

temperature reference sensor. The temperature coefficient of resistance (TCR) of the micro hotplate was obtained by an actual measurement of the resistance variation with increased temperature in a furnace. The value obtained of the TCR is 1.61×10^{-3} K^{-1}. The TCR of the micro hotplate is lower than the TCR of bulk Pt as the thickness of the micro hotplate is only 2 μm.

Figure 5 shows the sensing properties of the SnO_2 based micro hotplate gas sensor in H_2 gas concentrations of 50~20,000 ppm. It is noticeable that the gas is highly sensitive in response to a H_2 concentration as low as 50 ppm. We found a nonlinear relationship between the resistance and the hydrogen concentration of up to 20,000 ppm of hydrogen. The highest sensitivity of the gas sensor was obtained 4.8 at the concentration of 20,000 ppm.

The sensing mechanism of SnO_2 to H_2 gas can be divided into two parts. One part is the chemisorptions of O_2 species on to the surface of the SnO_2. Another part is the reaction of H_2 with the surface leading to a change in the properties of the SnO_2 involved. Under the presence of O_2 in the atmosphere, the sensing material chemisorbs it on its surface. O_2 can be adsorbed in several forms such as O_2^-, O^-, and O^{2-}. The interaction between a semiconductor surface and H_2 with reducing properties can be explained in terms of the reaction of H_2 molecules with the pre-adsorbed O_2.

The interaction between chemisorbed O_2 and the reducing gas H_2 results in a decrease of surface chemisorbed O_2 and in an increase of electrical conductance. An important factor to be taken in to account is the presence of the O_2 species on the sensor surface since the formation of hydroxyls is in competition with the O_2 adsorption; the OH^- group does not directly influence the surface reactions but affects the reaction rate.

Figure 6 shows the sensitivities of the SnO_2 based micro hotplate gas sensor at 300 °C to other gases such CO 500 ppm, H_2S 20 ppm, CH_4 25000 ppm, and H_2 2000 ppm. The sensitivity (S) is defined:

$$S = R_s - R_o/R_o \tag{3}$$

where R_s is the resistance of the sensing material and R_o is the base resistance in ambient air. The high sense response to H_2 gas seems to be Pd as a catalyst presence. The reaction product leaves the surface and enters the gas phase. The H_2 chemisorption is the rate-limiting step. In order to enhance the surface properties of the SnO_2, we introduced Pd as such a catalyst. The most important effects of the metal catalyst are the increase of maximum sensitivity and the rate of response.

4. CONCLUSIONS

In this paper we described the fabrication processes and the gas characterization of a MEMS based hydrogen gas sensor. The SnO_2 gas sensor with the micro-hotplate showed good response to the H_2 gas at 50~20,000 ppm and high selectivity H_2 gas as compared to other gases as CO, H_2S, and CH_4. Mass productivity of batch process type which is a merit of semiconductor fabrication method is still applied to SnO_2 gas sensor with micro hotplate so that manufacturing cost can be lowered.

Acknowledgments: This work was supported by the Hydrogen Energy R&D Center, one of the 21st Century Frontier R&D Programs, funded by the Ministry of Science and Technology of Korea, NRL (R0A-2007-000-20111-0) program of the Ministry of Science and Technology (Korea Science and Engineering Foundation).

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