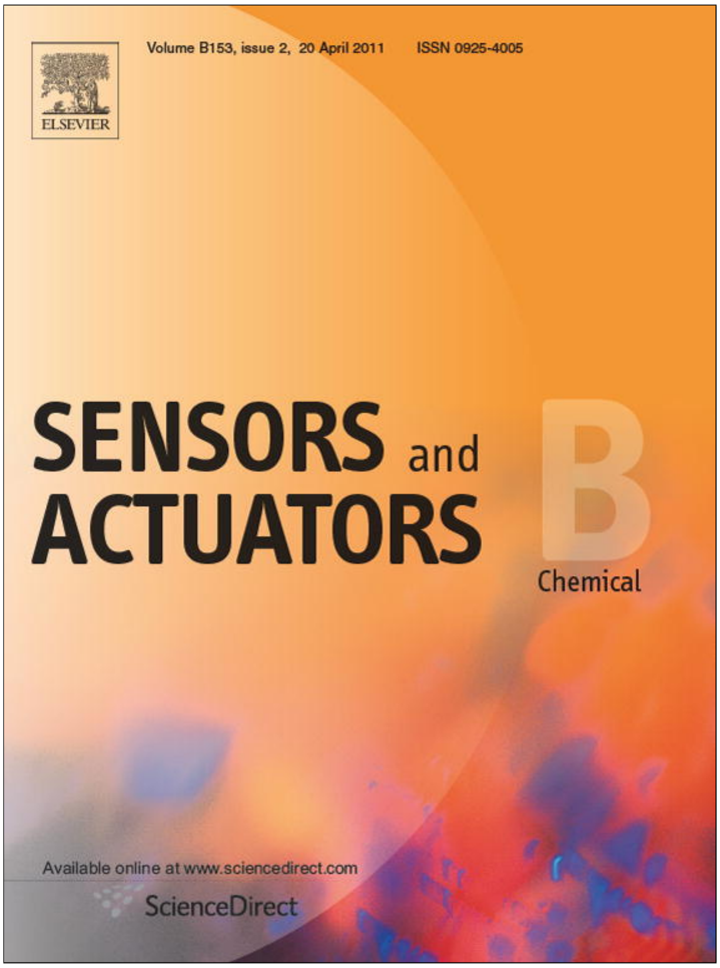
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Micromachined catalytic combustible hydrogen gas sensor

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ABSTRACT

An integrated catalytic combustion H_2 sensor has been fabricated by using MEMS technology. Both the sensing elements and the reference elements could be integrated into the suspended micro heaters connected in a suitable circuit such as a Wheatstone configuration with low power consumption. Two sensitive elements and two reference sensors were integrated together onto a single chip. The size of chip was 5.76 mm^2 and the catalytic combustion sensor showed high response to H_2 at operating voltage of 1 V. The response and recovery times to 1000 ppm H_2 were 0.36 s and 1.29 s, respectively.

1. Introduction

Various types of chemical gas sensors have been developed in order to detect toxic gases, which can be classified into three categories according to their sensing mechanism: electrochemical sensors, catalytic combustion sensors, and semiconductor gas sensors [1]. Catalytic combustion gas sensors have been widely used for many years to detect flammable gases or flammable vapor. Modern catalytic gas sensors called as "pellistors" was suggested by Baker [2]. Typically, the Pt coil is covered by catalyst-impregnated alumina bead and the temperature rise by combustion reaction is measured via the increase in the resistance of Pt coil [3–5].

Catalytic combustion gas sensors are now commercially available and mainly used as methane detectors for coal mining security [6]. It is advantageous to get high gas response with no influence water vapor, but high power consumption, a very low internal resistance, high cost and low reproducibility are the major challenges to overcome [7,8]. The slow response due to the poor ratio of sensing surface to mass should be also resolved. To detect combustible gases, the catalytic combustion sensors are usually heated to ~500 °C using Pt wire and the electric power for heating ranges from 300 to 700 mW. Therefore, the catalytic combustion sensors with low power consumption are very important for the longer operation of sensor using battery.

Micro-electromechanical systems (MEMS) technology is very attractive integrating and fabricating method as building block in the application of gas sensors. MEMS-based gas sensors, which have a small volume, low power consumption, low manufacturing cost for mass production, showed good gas sensing performance such as high gas response, fast response and recovery times [9–12]. In particular, the miniaturization of catalytic combustion gas sensors using MEMS technology is a promising solution to decrease the power consumption significantly. To date, many catalytic combustion gas sensors in the integrated form have been fabricated using thin film or micromachining techniques [13–15], which include the CH_4 sensor with the heater power of 100–250 mW [13], flammable gas sensors with the heater power of 100 mW [14]. Besides catalytic combustion type, thermoelectric type of H_2 sensor has been also proposed to reduce the sensor operation temperature [16].

H_2 is being widely used in industry, such as chemical production and fuel cell technology. Thus, the reliable and efficient detection of H_2 is very important to avoid any disaster from flammable and explosive H_2 [17]. In this contribution, an integrated design of catalytic combustion H_2 sensor with low power consumption has been designed and fabricated using MEMS technology. For the thermal insulation, the suspended micro bridge design is employed. In the sensors with a Wheatstone bridge, the sensor signal of two sensing elements configuration is 2 time higher than that of the single sensing element configuration [18]. Thus, in the present study, two the sensing elements and two reference elements are coated on the four suspended micro heaters with a Wheatstone configuration. To the knowledge of authors, this is the first report to fabricate the combustion type gas sensors with two sensing elements

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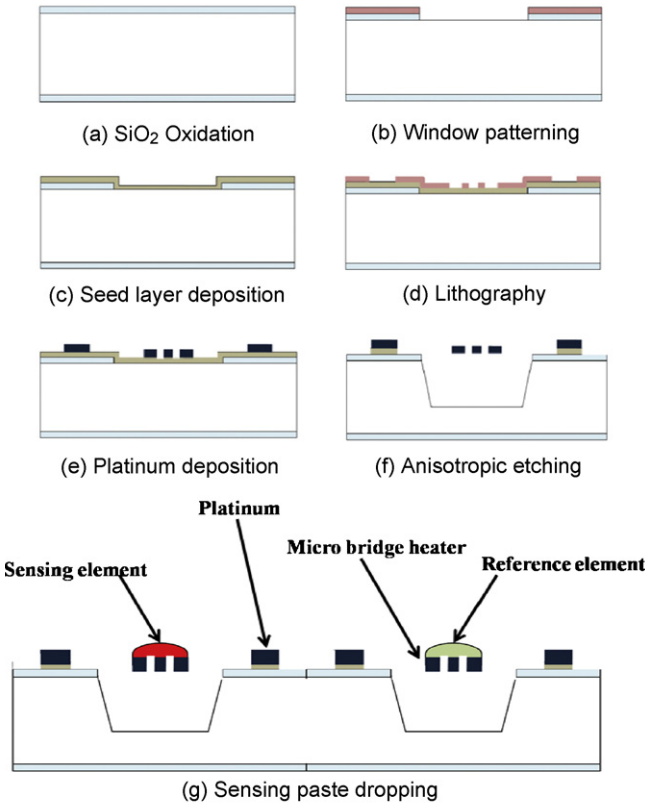

Fig. 1. Fabrication process flow for the catalytic combustion gas sensor.

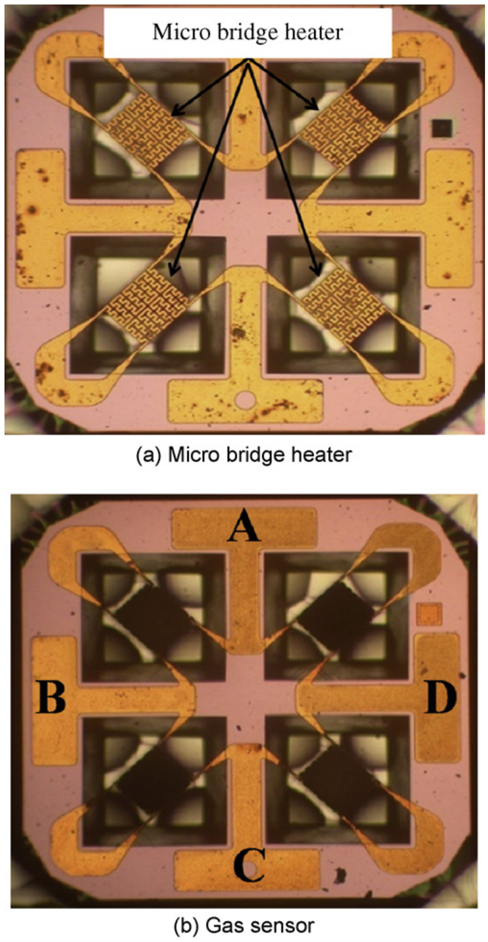

Fig. 2. A photograph of the fabricated sensor device (a) micro bridge heater and (b) gas sensor.

and two reference elements using MEMS technology. The fabrication process uses only two photo masks, which provides a simple and cost-effective approach to fabrication MEMS-based catalytic combustion sensor in a mass-production scale. The sensor with 2.4 mm × 2.4 mm in area selectively detects the low concentration of H_2 (20 ppm) with low total power consumption 55.68 mW. The sensor shows the responses in proportional to H_2 concentration and rapid response and recovery kinetics at the heater voltage of 1 V.

2. Experimental

2.1. Sensor preparation

The catalytic combustion gas sensors for H_2 has been fabricated on silicon wafers via the fabrication processes shown in Fig. 1. The substrate for the sensors device is a 4 in. n-type silicon wafer with a thickness of 520 μm and resistivity of 1–10 Ω cm. The substrate should be a good heat conductor and a good electric insulator. The Si wafers coated with silicon dioxide and silicon nitride are very suitable for integration with other components or for micromachining. After a standard cleaning procedure, a silicon dioxide film of ∼1.6 μm was deposited by thermal oxidation at 1100 °C. A photoresist was spin coated and then the window was patterned by exposure and development. An adequate hardbake process is important for the stability during the subsequent processing. The first mask was patterned in the onside of the substrate and the window was defined. A standard lithographic process was employed to pattern the cavity to be isolated and a Ti/Au seed layer for the electroplating was deposited by an E-beam evaporator. The thicknesses of the Ti and Au were 50 and 100 nm, respectively. An AZ 5214 photoresist is patterned on the seed layer, while the pure platinum layer is grown by an electroplating method. The thickness of the electroplated platinum film was 2.8 μm. Subsequently, the seed metal stripping is performed in wet etching solution and the front side of heater was removed by anisotropic etching to form a micro bridged structure. Fig. 2 showed the photograph of the fabricated gas sensor. The micro bridge heaters were used to heat the sensing elements and reference elements electrically to their operating temperature. And the sensor signal was measured between the heater. The temperature of the Pt heater at a given heater voltage was measured by observing the melting of temperature-sensitive crayons. In order to reduce the power consumption required to heat the sensor, the region on the side of the sensor was anisotropically etched using KOH solution onto the micro bridge heater of 2.5 μm in thickness. The micro heaters are suspended across a 200 μm deep cavity by platinum bridges and the area of the micro heater is 200 μm × 200 μm. The line width of the platinum bridge is 10 μm and the dimension of our sensor is 2.4 mm × 2.4 mm.

2.2. Sensing element

Catalytic combustion type sensors have gas sensing elements and compensation elements. To increase the response to H_2 and the number of detectable molecules, a catalyst such as platinum was added. The catalytic effects play an important role in improving the response to target gases and this is important for catalytic combustion type gas sensor. As sensing elements, the commercial γ-alumina (Sigma–Aldrich Co., Ltd.) was used. The 5 wt% Pt was loaded by the impregnation with H_2PtCl_6 (Heesung Metal., Ltd.) solution. In order to fabricate slurry containing sensing materials, the γ-alumina (reference element) and Pt loaded γ-alumina (sens-

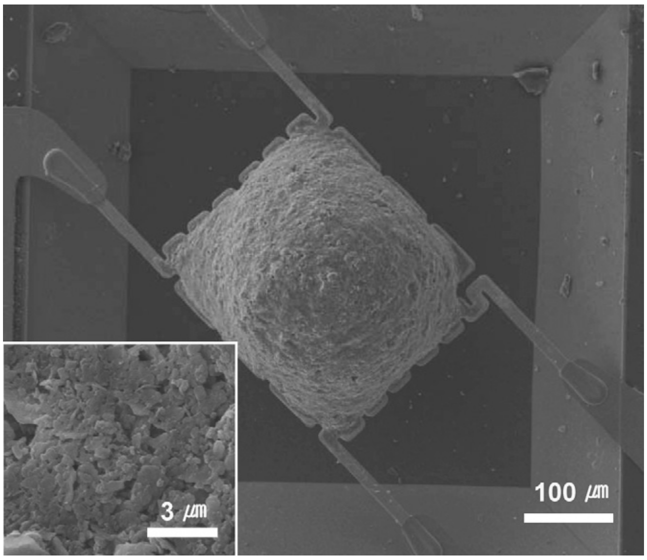

Fig. 3. A SEM image of the surface morphologies of the sensing layer.

ing element) powders were blended with 30 wt% of organic binder and then were dropped on the suspended micro heater using air dispenser and baked in air at 300 °C for 1 h. The element made of γ-alumina alone was used as the reference elements. Fig. 3 showed the surface morphologies of sensing layer. Well-defined deep silicon cavity is observed and the micro heater coated with sensing layer can be clearly seen. The sensing layer showed the polycrystalline nature with grain sizes less than 2 μm, which leads to an increase of the effective surface area. The highly refined grain size of the sensing layer was advantageous in enhancing the characteristics of the H_2 gas sensor.

2.3. Measurement

The catalytic combustion gas sensor was set in a temperature and humidity controlled test chamber and connected with a power supply. Fig. 4 showed the schematics of the bridge circuit for the catalytic combustion gas sensor. The H_2 concentration was adjusted from 20 to 30,000 ppm by the injection of dilute H_2 (air balance) to the chamber. The humidity was raised by flowing air through a heated water bubbler into the test chamber and was lowered using dry air. The humidity was measured with a portable humidity meter. The multimeter was used to record the output voltage of the sensor and to control the applied voltage. The collected data are analyzed by a DAQ (Data acquisition) which provided a graphic display of the results.

The gas response (ΔV) of the gas sensor developed in this study is given by the follow formula

$$\Delta V = V_{\text{output}} - V_{\text{offset}} = \left[\frac{\Delta R}{2(R_s + R_r)}\right] \times V_{\text{in}} \qquad (2\text{-}1)$$

where V_{output} and V_{offset} are measurement values of voltage upon exposure to air or H_2, ΔR is the change in the resistance of the heater, R_s and R_r are the values of the resistances of the sensing element and the reference element, respectively. V_{in} is the applied voltage. That is, Rs is $R_0 + \Delta R$ and R_r correspond to R_0. Therefore, the gas response, ΔV is defined as the difference between the output voltage in air containing H_2 (V_{output}) and the offset voltage in air (V_{offset}).

Here, ΔR was expressed by the following equation

$$\Delta R = \frac{\alpha \times m \times Q}{C} \qquad (2\text{-}2)$$

where α is a constant, which is the temperature coefficient of the metal material of the heater, m is the concentration of the combustion gas, Q (J/mol) is the combustion heat of the gas molecules, and C (J/cm^3 K) the heat capacity of the sensor. The combustion gas sensor is worked by burning the target gas. The heat generated by catalytic combustion reaction changes the resistance of the sensor in proportional to the gas concentration. To obtain high response, the catalytic combustible sensor should have a high temperature coefficient of heater resistance and a smaller heat capacity as shown in Eq. (2-2). In combustion type gas sensors, the heat generated by combustion reaction will be radiated directly from the sensing part to the ambient atmosphere or can be transferred to the neighboring substrate. In either case, to make the sensor more sensitive, the heat loss should be minimized. In this study, the former heat loss was decreased by making Pt heater as well as combustion region within a small volume and the latter heat loss was minimized by

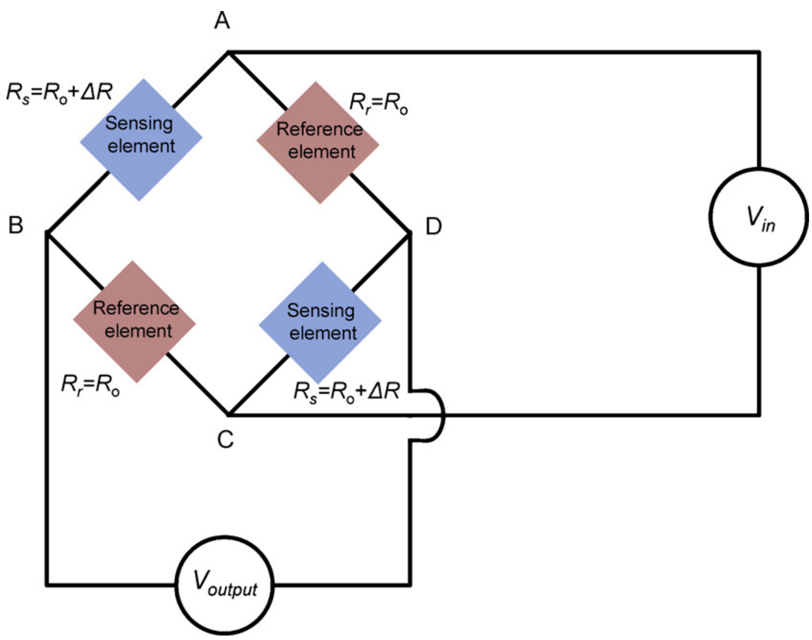

Fig. 4. Schematic of the bridge circuit of the catalytic combustion gas sensor.

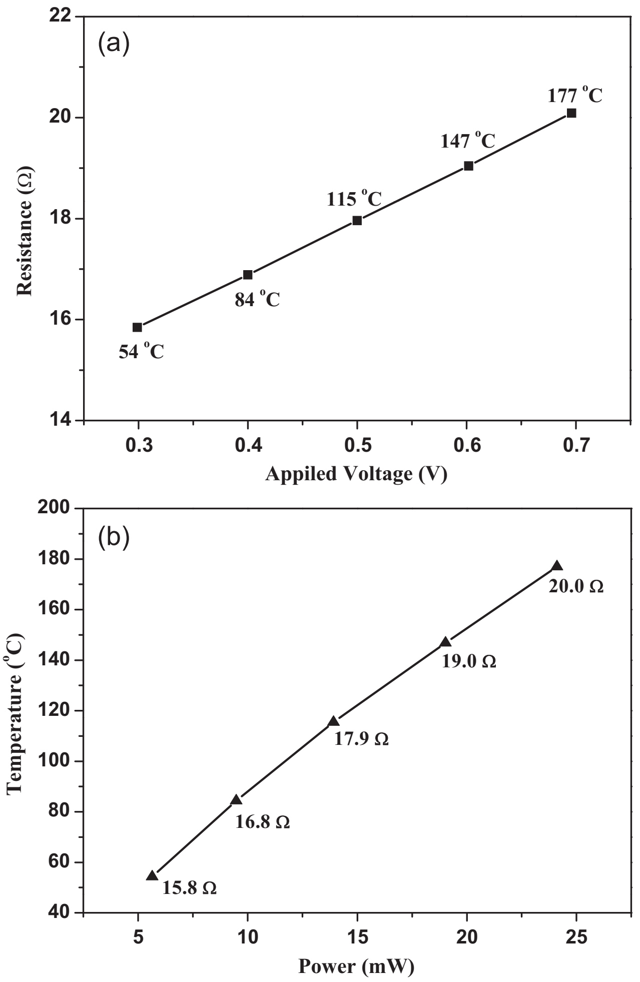

Fig. 5. (a) The resistance of single microheater as a function of applied voltage and (b) the temperature of single microheater with varying heater power.

the thermal isolation of sensing and reference part using suspended electrode design.

3. Results and discussion

3.1. Electrical and thermal properties

The electrical and thermal properties of the sensing element have been studied. For the temperature coefficient of resistance (TCR) measurement the sensor device was introduced in a precisely controlled oven and the resistance was measured after achieving the required temperature stabilization. In the sensor with Wheatstone configuration, typically, 1 V was applied to sensor, which corresponds to the application of 0.5 V for each microheater. The resistance of single Pt microheater was measured as a function of applied voltage (Fig. 5(a)). The present micro bridge heater has a resistance R that depends linearly on its absolute temperature T, namely,

$$R(T) = R(T_o)[1 + \alpha(T - T_o)] \tag{3-1}$$

where, $R(T)$ and $R(T_o)$ are the resistance of the micro hotplate at temperatures T and T_o, respectively, and α is the linear temperature coefficient of the resistance (TCR). The calculated TCR of the sensor with the micro platinum heater was 3445 ppm/°C. The TCR of the typical industrial platinum resistance thermometers (IPRTs) was 3850 ppm/°C [19]. The TCR value in this study is in good agreement with that of the IPRTs.

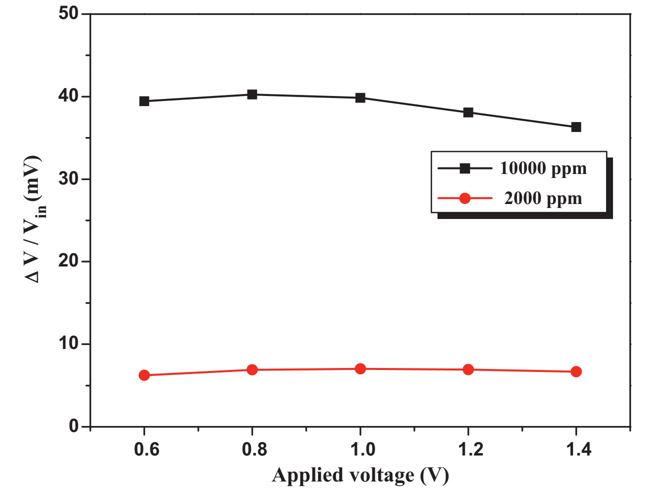

Fig. 6. Sensing signal of the gas sensor to 2000 and 10,000 ppm H_2 as a function of the operating voltage.

3.2. Sensing characteristics

Fig. 5(b) showed the temperature variation of the single microheater as a function of applied power where it can be seen that as the power increases, the temperature of the sensing element

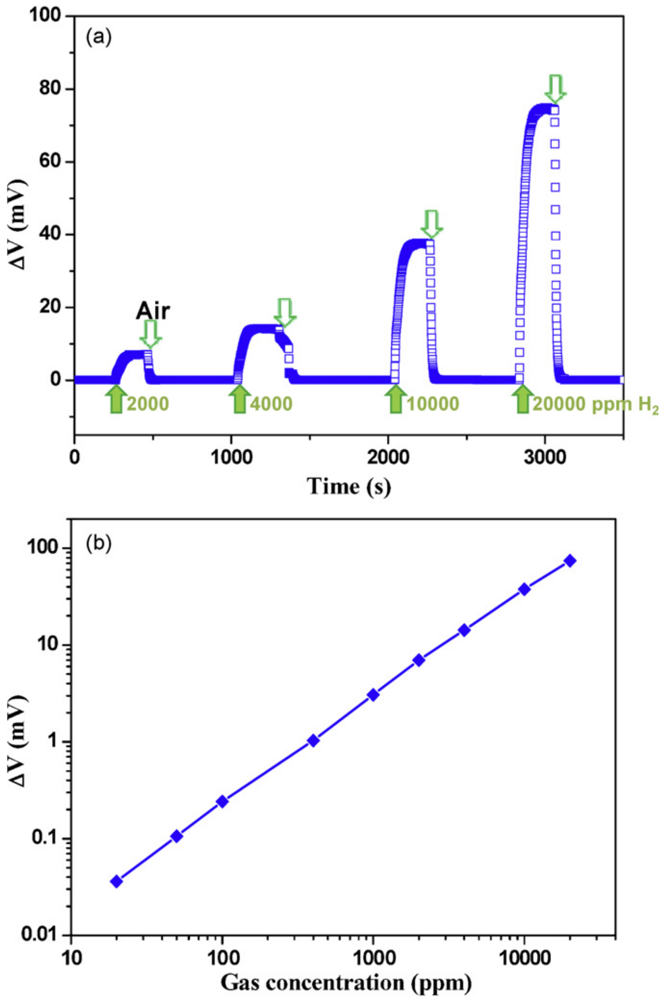

Fig. 7. (a) Dynamic sensing transients to 2000–20,000 ppm H_2 at the applied operating voltage of 1 V and (b) sensor signal as a function of H_2 concentration.

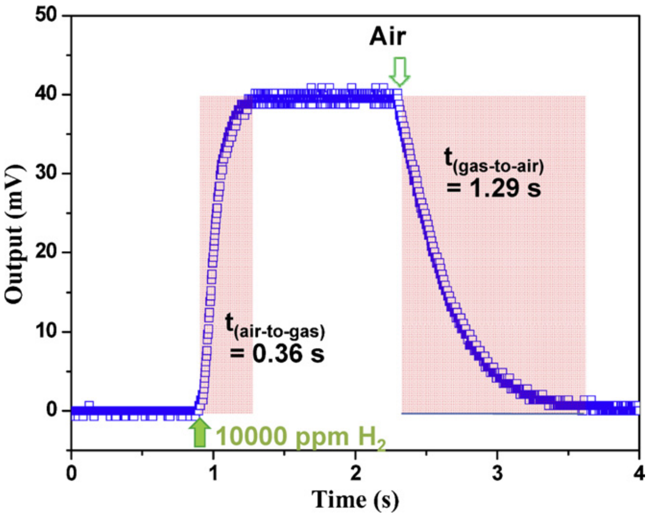

Fig. 8. Response and recovery times of the sensor to 10,000 ppm H_2 at operating voltage of 1 V.

increases. At the applied voltage of 0.5 V, the power consumption was only about 13.92 mW and the sensor temperature was 115 °C. Thus the total power consumption at the sensor temperature of 115 °C (V_{in} = 1.0 V) is 55.68 mW. This low level of power consumption is due to the superior thermal insulation provided by the suspended configuration and is an advantage of the present MEMS-based gas sensor. It is important for portable applications which are dependent on the power consumption. The $\Delta V/V_{in}$ values to 2000 and 10,000 ppm H_2 were attained as a function applied voltage (Fig. 6). At high voltage (1.2–1.4 V), the sensor stability was deteriorated probably due to the excessive heating of sensing element. When the hydrogen concentration is low (2000 ppm) the signal variation was not significant. However, at the higher H_2 concentration (10,000 ppm), the highest sensor signal could be attained between 0.8 and 1 V. So we operated the sensor at 1 V. Gas sensing characteristics to various concentration of H_2 have been estimated. The humidity and temperature of the gas mixture were controlled to about 20% RH and 20 °C, respectively. At the applied voltage of 1 V, the response values (ΔV) to 20–20,000 ppm H_2 increased from 0.036 to 74.5 mV in Fig. 7. These values were proportional to the concentration of H_2. The sensor signal recovered to air level stably, which indicates that the combustion process of H_2 in the sensing element was reversible.

The 90% response and recovery times upon exposure to 10,000 ppm H_2 and air were calculated from the dynamic sensing transients (Fig. 8), which were 0.36 and 1.29 s, respectively. This shows that the present sensor react to H_2 instantaneously and can recover within a short time. The small size and thermal mass might facilitate the rapid sensing and recovery. The gas responses to H_2, C_4H_{10}, CH_4, C_2H_5OH, C_3H_8, C_6H_{14}, and DME (dimethyl ether, CH_3OCH_3) were also investigated (Fig. 9(a)). The response to H_2 was markedly higher than those for other gases. Finally, the sensor signal was very stable during the long term operation (for 248 days) (Fig. 9(b)). The characteristics clearly show that the MEMS-based catalytic combustion gas sensor in this study can detect H_2 in a selective and reliable manner with rapid response speed.

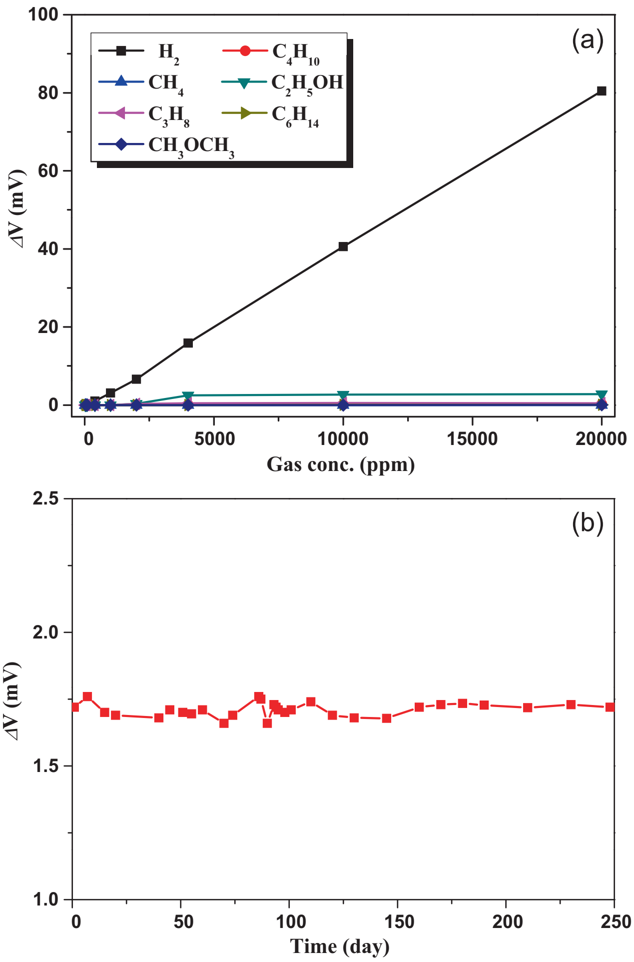

Fig. 9. Selectivity and (b) long-term stability of the sensors at operating voltage of 1 V.

4. Conclusion

It has been shown that a catalytic combustion H_2 sensor can be manufactured with MEMS technology. Photolithography and bulk micromachining techniques, such as KOH etching, have been used to fabricate the micro bridge gas sensor. The main advantages of this work are the integration of two sensitive sensors and two reference sensors on to one chip connected in a suitable configuration such as a Wheatstone bridge circuit. The power consumption was very low (55.68 mW) to operate the catalytic combustion sensor at 115 °C, which can be attributed to the small size of microheater and the superior thermal insulation provided by the suspended configuration. The fabricated catalytic combustion gas sensor possesses relatively high response, selectivity, rapid response/recovery and high reproducibility of the output signals. Moreover, in this study, the present gas sensor can be used in realizing portable sensing devices such as gas analyzers and gas leak detectors.

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