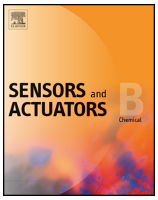
Sensors and Actuators B 249 (2017) 571–580

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb



Heat transfer control of micro-thermoelectric gas sensor for breath gas monitoring

Tomoyo Goto[a,1], Toshio Itoh[a], Takafumi Akamatsu[a], Yoshitaka Sasaki[a,b], Kazuo Sato[b], Woosuck Shin[a,*]

[a] *National Institute of Advanced Industrial Science and Technology (AIST), 2266-98 Shimo-Shidami, Moriyama-ku, Nagoya 463-8560, Japan*
[b] *Aichi Institute of Technology, 1247 Yachigusa, Yakusa-Cho, Toyota 470-0392, Japan*

ARTICLE INFO

Article history:
Received 14 October 2016
Received in revised form 13 March 2017
Accepted 19 March 2017
Available online 23 March 2017

Keywords:
Gas sensor
Catalyst
Thermoelectric device
Micro-electromechanical systems (MEMS)
Finite element method (FEM)

ABSTRACT

A micro-thermoelectric gas sensor (micro-TGS) uses thermoelectric voltage induced by the catalytic combustion of hydrogen or methane for selective gas detection in breath. This is accomplished under an elevated temperature using a micro-heater built on the same membrane as a hotplate, which enables selective combustion of the target gas. A temperature differential built by the catalyst on the membrane induces the offset voltage (V_{off}) of the micro-TGS, which limits the amplifier circuit application. In this study, we strived to suppress V_{off} by an additive integration process of heat dissipation dots prepared using α-Al_2O_3 paste. In this paper, we discuss the effects of these α-Al_2O_3 dots on the thermal balance over the micro-TGS membrane by finite element method (FEM) modeling. When the dots were deposited in a symmetrical position to the combustion catalyst, V_{off} was compensated depending on the size, numbers, and locations of the dots. The micro-TGS heat transfer control by the dots was additionally verified by 3-D FEM modeling. The changes in V_{off} by the α-Al_2O_3 dots in FEM modeling were greater than those of the experiments, suggesting the high thermal conductivity of the micro-TGS membrane. The deviation of the membrane thermal conductivity due to the process non-uniformity significantly influenced the V_{off}; however, it was effectively reduced by the additive integration of dots.

1. Introduction

Medical diagnostic technologies for early disease stages have been widely studied in response to global population aging issues and the expansion of the health care industry. Among these technologies, breath analysis techniques have garnered considerable attention as non-invasive and simple health check methods that can be conducted both at home and in a medical facility. Human breath includes several kinds of inorganic and volatile organic compounds (VOCs). These gases are known as markers of disease and human body metabolism [1,2]. To detect the part-per-million (ppm) levels of breath gases, such as H_2, CO, and CH_4 [3], we developed a unique micro-thermoelectric gas sensor (micro-TGS) with various combustion catalysts for a breath analysis system.

Calorimetric gas sensors take advantage of micro-machined devices using the heat of the chemical reactions generated by catalytic metals. Their thermal characteristics must be optimized for better sensing performance. The micro-TGS uses the catalytic combustion of the gas operated at a catalyst temperature over 100 °C by using a micro-heater built on the membrane. It thereby shows the linear relationship of the voltage signal to the gas concentration [4,5] and the sensing performance for the ppm level of hydrogen in the breath gas analysis [5]. Sensor performance of micro-TGS, a synergistic combination of the catalytic combustion of gas and thermoelectric conversion (from heat to electrical), can be easily modulated by the choice of the combustion catalyst.

Previously, micro-TGS for H_2, CH_4, and CO detection were reported using Pt/α-Al_2O_3 [4,5], Pd/θ-Al_2O_3 [6], and Au/Co_3O_4 [7] catalysts, respectively. To produce an effective design, the heat balance of the sensor during operation must be estimated. The heat balance can predict the inflammable gas combustion energy of the catalyst. The heat as a function of the sensor output is also important for the development of the catalyst.

The membrane area of the micro-TGS is comprised of ends of thermoelectric SiGe forming a symmetrical pattern. However, one end of the SiGe pattern is covered by a ceramic combustor (combustion catalyst), which induces the asymmetrical temperature

---

* Corresponding author.
E-mail address: w.shin@aist.go.jp (W. Shin).
[1] Present address: The Institute of Scientific and Industrial Research (ISIR), Osaka University, 8-1 Mihogaoka, Ibaraki 567-0047, Japan.

http://dx.doi.org/10.1016/j.snb.2017.03.113
0925-4005/

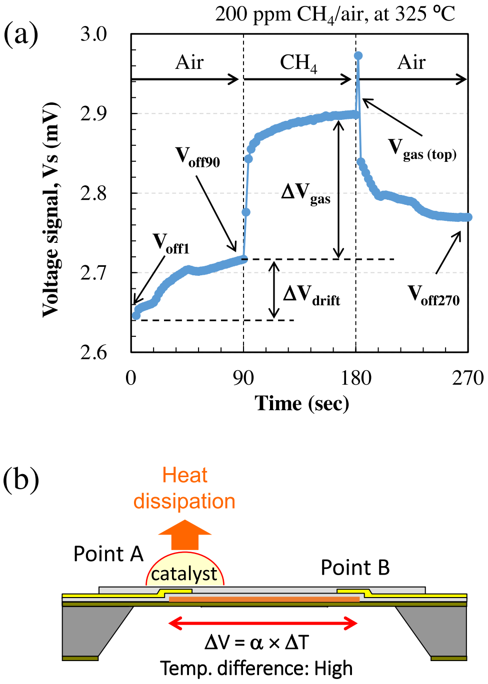


Fig. 1. (a) Voltage signal (Vs) of micro-TGS for detection of CH_4 and (b) schematic illustration of the micro-TGS.

distribution in the membrane and results in the temperature differential, as shown in Fig. 1. Fig. 1(a) depicts an example of a voltage signal of micro-TGS for detection of CH_4 at 325 °C. It indicates a problem of micro-TGS in real applications; i.e., voltage from the sensor from the initial stage in air, named the offset voltage (V_{off}), occurs at a high temperature operation. The fluctuation or drift of the V_{off} can also be a serious problem when the target gas concentration is low. The voltage signal was thus gradually elevated after 90 s (V_{off90}) from the initial stage (V_{off1}). This difference of V_{off} is shown in ΔV_{dirft} in Fig. 1(a). After CH_4 detection, the voltage continues to rise, and the offset voltage at 270 s (V_{off270}) is higher than that of the initial stage (V_{off1}).

The origin of this problem was an initial temperature difference (ΔT) formed between point A (catalyst site) and point B:

$$V_S = \alpha \cdot \Delta T_{AB} = \alpha \cdot (T_A - T_B) \tag{1}$$

where α is the Seebeck coefficient of the thermoelectric film. This V_{off} of micro-TGS increases in high temperature operation because the combustion catalyst on the membrane plays the role of "heat dissipater" (Fig. 1(b)). In addition, non-uniformity of the membrane in micro-TGS also effects the heat balance inside the membrane.

Generation of this voltage cannot be ignored because the voltage signal increases with the increasing operating temperature. The suppression of offset voltage of micro-TGS is important to stabilize the base voltage and improve the quantitative performance. To make an effective design of each part of micro-TGS, especially the catalyst and micro-heater, meanders are important for optimizing the sensor performance. To make effective design of each parts of micro-TGS, especially a double meander-shaped Pt heater and a circular shape catalyst are important to optimize the sensor performance, and moreover it is important to quantitatively evaluate the heat transfer of these parts.

Optimization of the micro-heater can involve thermal distribution in the membrane that is aimed at temperature control of a uniform and stable response at elevated temperatures, thereby improving the sensor reliability and sensitivity. The development of a theoretical model for thermo-mechanical calculations and heat transfer mechanisms is important for the design of catalytic sensors, which can include predicting device process non-uniformity. The influence of the micro-hotplate design on the catalytic reaction or sensor response is not fully understood, the model calculation is expected to be effective tool for the sensor development. Most studies have primarily focused on flowmeters [8], while heat and mass transfer in heated systems [9] and thermochemical devices in gas-fueled combustor systems [10] have additionally been investigated.

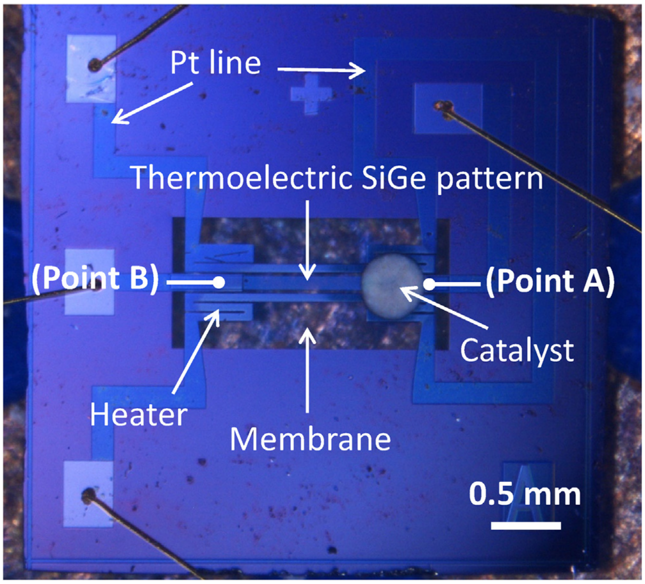


Fig. 2. Optical image of the micro-TGS.

In the case of micro-TGS, the heat of gas combustion at the catalyst film which is thin and smaller than 1 mm, is extremely difficult to directly measure. In our previous study, however, we have quantitively estimated the catalytic combustion heat (power) required for 1 mV of signal voltage to be 46 μW, using the linear calculation and thermal time constants of the experimental signal curves of the micro-TGS [11]. The design of micro-heater meanders can efficiently and uniformly heat the catalyst; moreover, they can prevent the loss of combustion heat though the heater line. Various heater designs have been tested. The power consumption of the micro-heater meanders was reduced to 30–40 mW at the catalyst temperature of 100 °C, which is approximately 30% less than that of the first generation one [12]. In addition, an asymmetric micro-heater meander enabled different catalyst temperatures for a single sensor with a double catalyst structure.

In this study, to control this heat balance and suppress V_{off} of micro-TGS, the α-Al_2O_3 thick film, dummy dots, for heat dissipation were additively integrated on the membrane of micro-TGS. The effects of the α-Al_2O_3 dots on the heat balance are herein described with the quantitative results estimated by 3-D solid modeling of the finite element method (FEM). The effects of thermal conductivity of micro-TGS on the V_{off} control by α-Al_2O_3 dots are then discussed.

2. Experimental

2.1. Design of micro-TGS

Details of the preparation procedure of micro-TGS for H_2 and CH_4 detection were described in previous reports [4–6]. Here, the p-type B-doped SiGe thermoelectric pattern was used for the micro-TGS device. As shown in Fig. 2, the $4 \times 4\,mm^2$ dimension of the micro-TGS device was comprised of the thermoelectric pattern, Pt heater, and electrode line pattern on a double-sided polished Si substrate. The optimal geometrical design comprised of the