Metal Oxide Semiconductor Sensors for Acetone Detection with Hot Wire Type Structure

Tatsuya Ohishi*, Shoichiro Nakao*, Takafukmi Taniguchi*, Hirokazu Mitsuhashi*, Takeshi Eda† and Tomohiro Kawaguchi†
Email: nakao.shoichiro@new-cosmos.co.jp
*New Cosmos Electric Co., Ltd., Osaka, Osaka, Japan
†Figaro Engineering Inc., Mino, Osaka, Japan

***Abstract*—We present an affordable metal oxide semiconductor sensor suitable for acetone detection below 1 ppm. The sensor has a unique structure, in which components are only bare essentials: a coil of noble metal for both heating and measuring, a semiconductor bead for detecting acetone, and a catalytic overlayer for removing interference gases. The sensor exhibited good sensitivity to acetone together with selectivity over ethanol and hydrogen. These properties were retained for more than two years in a laboratory environment, demonstrating excellent long-term stability of the sensor.**

Keywords—metal oxide semiconductor, hot wire type structure, acetone, breath analysis

I. Introduction

Acetone concentrations in human exhaled breath strongly correlate with metabolism, and are potentially used for non-invasive monitoring of human health [1]. For example, many studies were carried out to detect diabetes with breath acetone sensing for this decade [1, 2]. In addition to the use as a diabetes biomarker, guiding the ketogenic diet with breath acetone sensing shows a promise of widespread use [3]. The most important technical challenge for this purpose is to detect dilute acetone selectively in human exhaled breath, in which extremely high relative humidity (RH) and various gases such as ethanol and hydrogen hinder acetone sensing. Note that targeted concentrations of acetone are around 1 ppm, whereas the concentrations of the interference gases might be as high as 100 ppm. A precise but costly approach is to build a system that can separate acetone from interference gases by using gas chromatography or specially designed catalyst-filtration [1, 4]. For widespread use, however, a more affordable approach is highly desirable.

Recently, tremendous advances in data processing technologies like machine learning have made it possible to detect acetone selectively even by combining affordable commercial sensors [5, 6, 7]. We believe that such sensors support the basis of interdisciplinary studies. One of the sensors used in such studies is TGS1820 (TGS1820-A00, Figaro Engineering Inc.), which has been developed to detect acetone with good selectivity over interference gases. We are, however, aware that some studies reported that the sensor required further improvement in selectivity over ethanol [6] and stability against temperature and/or humidity fluctuations. In this work, we present various properties of an improved version of TGS1820. In addition, we include some remarks about practical use of the sensor for the aid of the scientists outside of material science.

II. Experimental

Fig. 1(a) shows schematics of the sensor structure. The sensor detects reducing gases as a change in the electric resistance of metal oxide semiconductor (MOS). Typical MOS sensors with a thick film structure require an interdigitated electrode for sensing and another electrode for heating. In contrast, the sensor in this work has a unique structure [8], in which components are only bare essentials: a coil of noble metal used for both heating and measuring, a MOS bead embedding the coil for detecting acetone, and a catalytic overlayer on the bead for removing interference gases selectively. The simple and symmetric structure enables us to heat sensors efficiently, coat MOS beads with catalytic overlayers nicely, and reduce production costs. The structure has been referred to as a hot wire type structure, which has been adopted to fabricate sensor elements [9, 10] in products of New Cosmos Electric Co., Ltd. for more than 30 years.

Sensor output voltage (V_b) was measured with the Wheatstone bridge circuit, as shown in Fig. 1(b). Circuit voltage and load resistor values were set to DC 2.3 V and 10 Ω, respectively. Adherence to these values was very important because both values were selected to heat the sensor at an optimal temperature for various properties. Higher circuit voltage and lower load resistor than the standard values should be avoided because they might damage the sensor irreversibly due to excessive heating. In this work, we defined the difference between V_b in clean air (V_b(Air)) and V_b in gas mixture ambient (V_b(Gas)) as the sensitivity of the sensor ($\Delta V_{out} = V_b(\text{Gas}) - V_b(\text{Air})$). To stabilize V_b(Air), the sensors were energized in a given environment for one hour before measurements.

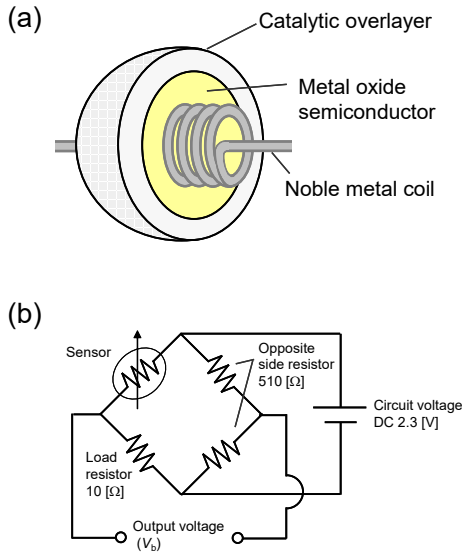

Fig. 1. (a) Schematic structure of the sensor element. (b) Basic measuring circuit for the sensor.

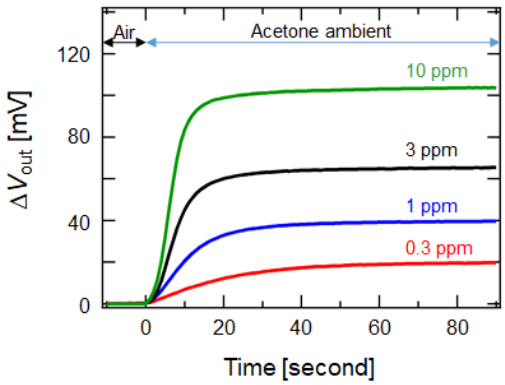

Fig. 2. Typical sensor response to acetone ambient with various concentrations.

III. Results and Discussion

Fig. 2 shows sensor response to acetone with various concentrations measured at 20 ℃ and 65 % RH. Obviously, the sensor exhibited a very quick response to acetone even lower than 1 ppm. Typical ΔV_{out} to 1 ppm acetone was approximately 40 mV, being sufficiently high for various applications. The sensor response almost got saturated within 60 seconds. Consequently, design of gas flow would be a limiting factor of response for most devices with the sensors.

Next, we discuss the acetone selectivity of the sensor over interference gases. Fig. 3(a) shows a comparison of the typical ΔV_{out} of the sensor to acetone with those to ethanol and hydrogen. Data for the sensor of previously released version are shown in Fig. 3(b) for comparison. The improved sensor exhibited good acetone selectivity over ethanol and hydrogen; ΔV_{out} to 1 ppm acetone was nearly equal to ΔV_{out} to 100 ppm ethanol and was almost twice higher than ΔV_{out} to 300 ppm hydrogen. In comparison with the previous sensor, the improved sensor showed enhanced sensitivity to acetone together with lowered sensitivity to ethanol and hydrogen. The improvement in selectivity was achieved by fine optimization of the structure, composition of the MOS bead, and operating temperature of the sensor.

The optimization not only improved the selectivity of the sensor but also reduced the effect of ambient humidity and temperature on the sensor properties. Figs. 4(a) and 4(b) respectively show the V_b(Air) and ΔV_{out} to 1 ppm acetone measured at various ambient temperatures and RH. Data for the previous sensor are also shown for comparison. The previous sensor suffered from fluctuation of V_b(Air) due to ambient temperature and humidity. As a consequence of optimizing the composition of the MOS bead, the fluctuation of V_b(Air) of the improved sensor was suppressed. We hope that more reliable results for breath analysis can be obtained by using the improved sensor in this work.

The effect of humidity on the sensing properties of MOS sensors is in general complicated and is still a matter of debate [11]. Empirically, moderate or rather high humidity is necessary for high ΔV_{out} of MOS sensors. Indeed, high ΔV_{out} was obtained at 65 % and 90 % RH, as shown in Fig. 4(b). On the other hand, use in dry ambient resulted in reduced ΔV_{out}. Fortunately, real samples for breath analysis are usually highly humid and are therefore suitable for acetone detection using the sensor in this work. Careful sampling might be necessary for model experiments using synthetic gases that contain very low humidity.

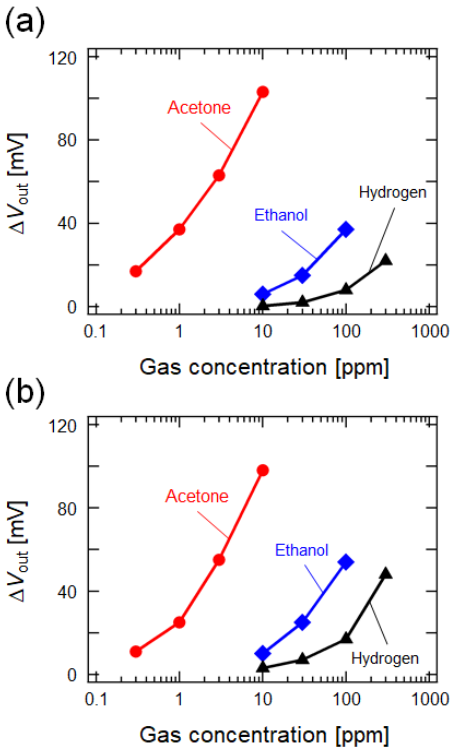

Fig. 3. Typical acetone selectivity over ethanol and hydrogen of (a) the improved and (b) the previous sensors.

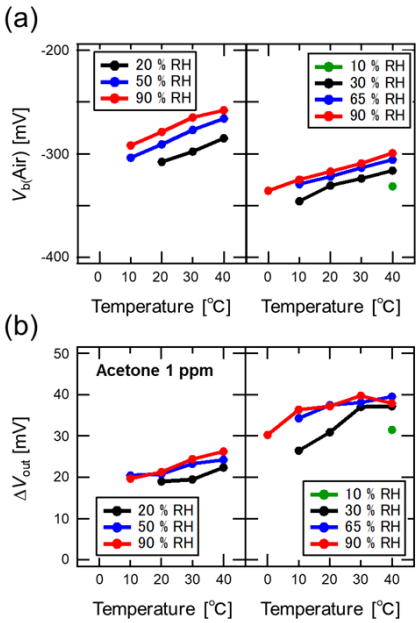

Fig. 4. Ambient temperature dependence of (a) V_b(Air) and (b) sensitivity to 1ppm acetone of the previous (left panels) and the improved (right panels) sensors measured at various RH.

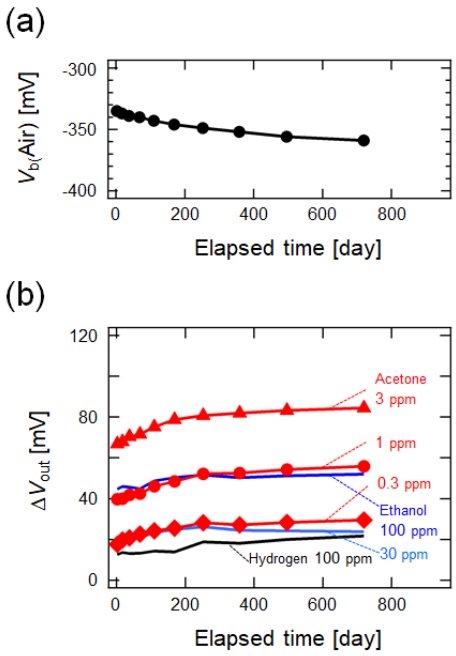

Fig. 5. Long-term stability of the sensor: (a) V_b(Air) and (b) sensitivity to acetone, ethanol, and hydrogen.

Practically, sensors not in use are usually unenergized. Unheated MOS surfaces easily adsorb water and volatile organic molecules, which compete with oxygen adsorption on the MOS surfaces after energizing. Because the adsorbed oxygen is the source of the sensor response of MOS to reducing gases, unenergized sensors for a long time require prolonged heating before use. Typically, energizing for one hour is sufficiently long to obtain the expected V_b(Air) and ΔV_{out}. It is practical to monitor V_b(Air) and wait for stabilization during energizing before use.

Finally, the long-term stability of continuously energized sensors in a laboratory environment (20 ℃ and 60 % RH) was tested, as shown in Fig. 5. For more than two years, the sensors exhibited high sensitivity to acetone, good selectivity over ethanol and hydrogen, and stable V_b(Air), albeit with slight drift. These results obviously demonstrate excellent long-term stability of the sensors. Unenergized sensors as well exhibited similar excellent long-term stability of sensing properties (data not shown). These excellent features make the sensor very promising for various applications such as breath acetone analysis and a component of multi-sensor arrays in electronic noses.

IV. Conclusions

In this work, we presented an affordable MOS sensor suitable for acetone detection below 1 ppm. The sensor had a unique structure, in which components were only bare essentials: a coil of noble metal used for both heating and measuring, a MOS bead embedding the coil for detecting acetone, and a catalytic overlayer on the bead for removing interference gases selectively. The simple and symmetric structure enabled us to heat sensors efficiently, coat MOS beads with catalytic overlayers nicely, and reduce production costs. The sensor exhibited a very quick response to acetone even lower than 1 ppm. Typical ΔV_{out} to 1 ppm acetone was approximately 40 mV. The sensor exhibited good acetone selectivity over ethanol and hydrogen; ΔV_{out} to 1ppm acetone was nearly equal to ΔV_{out} to 100 ppm ethanol and was almost twice higher than ΔV_{out} to 300 ppm hydrogen. The optimization for high ΔV_{out} reduced the fluctuation of V_b(Air) due to ambient temperature and humidity. High ΔV_{out} was obtained at 65 % and 90 % RH, being suitable for humid samples of breath analysis. For more than two years, the sensors exhibited high sensitivity to acetone and good selectivity over ethanol and hydrogen, demonstrating excellent long-term stability. These excellent features make the sensor very promising for various applications such as breath acetone analysis and a component of multi-sensor arrays in electronic noses.

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