A Study on Pattern Analysis of Odorous Substances with a Single Gas Sensor
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Abstract

This study used a single metal oxide semiconductor (MOS) sensor to classify the major odorous gases hydrogen sulfide (H₂S), ammonia (NH₃) and toluene (C₆H₅CH₃). In order to classify these odorous substances, the voltage on the MOS sensor heater was gradually reduced in 0.5 V steps 5.0 V to examine the changes to the response by the cooling effect on the sensor as the voltage decreased. The hydrogen sulfide gas showed the highest sensitivity compared to odorless air under approximately 2.5 V and the ammonia and toluene gases showed the highest sensitivity under approximately 5.0 V. In other words, the hydrogen sulfide gas reacted better in the low temperature range of the MOS sensor, and the ammonia and toluene gases reacted better in the high-temperature range. In order to analyze the response characteristics of the MOS sensor by temperature in a pattern, a two-dimensional (2D) x-y pattern analysis was introduced to clearly classify the hydrogen sulfide, ammonia, and toluene gases. The hydrogen sulfide gas was identified by a straight line with a slope of 1.73, whereas the ammonia gas had a slope of 0.05 and the toluene gas had a slope of 0.52. Therefore, the 2D x-y pattern analysis is suggested as a new way to classify these odorous substances.

Keywords: Metal oxide semiconductor (MOS), Odorous substance, Odor sensor, Temperature transient, PCA, 2D x-y pattern analysis.

1. INTRODUCTION

The methods for measuring or monitoring odors or odorous substances can be largely classified into four types, but the most popular methods involve measuring the concentration of each component of odors or odorous substances using the olfactory method of the human sense of smell or an analytical device. In addition to these, the gas sensor method and passive sampler method are new attempts to measure odors or odorous substances continuously over time and to measure their changes in space, respectively [1].

The odor monitoring method using a metal oxide semiconductor (MOS) gas sensor has been introduced as the most effective way of measuring odors because it can measure odors and odorous substances on the basis of both time and space, but there are many issues to resolve in order to measure both the intensity and the type of odors as effectively as the human sense of smell. In order to evaluate the type of odors, in particular, the electric nose system is being developed as an array of multiple sensors that work similar to human olfactory cells; however, few of sensors are applicable, and the system becomes more complicated and it is difficult to handle the signals from each individual sensor as more types of sensors are applied.

In order to mitigate the drawbacks of MOS sensors despite their exceptional responsiveness, there have been many studies on the application of catalysts and filters and building an array of multiple MOS sensors to interpret the response signals as patterns, but the studies on the electric nose system have reported little success because of the limitations of MOS sensor development. However, the characteristics of sensors according to temperature changes have been studied in various ways in order to improve the selectivity of MOS sensors [2-4].

Among the studies that have identified types of gas substances using the sensitivity differences for gas substances according to the MOS sensor temperature conditions sensors, Andrew et al. [5] showed that the sensitivity of a semiconductor gas sensor composed of SnO₂ and its compounds varies by temperature and Huang et al. [6] and Ngo et al. [7] showed that CO gas can be measured selectively by varying the temperature of a semiconductor gas sensor. Various studies have shown that gas...
substances can be identified by a single semiconductor gas sensor simply by changing its temperature.

In addition, Cho et al. [8] developed an electric nose system that classifies pseudo-petroleum using single semiconductor gas sensors and pattern analysis technology. Hiranaka et al. [9] and Gutierrez-Osuna et al. [10] conducted a study to examine the response of odorous substances while reducing the voltage of the sensor heater from high-temperature conditions to low-temperature conditions to compare the response characteristics of odorous substances according to the sensor temperature.

Vergara et al. [23,24] configured a MOS sensor on a micro-hotplate to make it easier to control the temperature of a MOS sensor and classified ammonia (NH\textsubscript{3}), ethylene (C\textsubscript{2}H\textsubscript{4}), acetaldehyde (CH\textsubscript{3}CHO), and nitrogen oxide (NO\textsubscript{2}) gases using the sensor temperature. The response signals of sensors by the sensor temperature showed that gas substances could be classified using a neural network algorithm called fuzzy ARTMAP. However, some of the drawbacks are that pattern analysis using this neural network needs a PC-grade hardware interface because it requires a sophisticated algorithm and at least hundreds of iterative data should be secured for the system to learn the patterns of odorous substances.

Therefore, this study changed the temperature conditions of a single MOS sensor to examine the difference of each odorous substance to the MOS sensor temperature on the basis of the MOS sensor response characteristics according to the major odorous gases of hydrogen sulfide, ammonia and toluene. Experiments were conducted to determine whether the differences in response according to the temperature conditions can be used to classify the odorous substances using the principal component analysis (PCA) method. In order to suggest a new method of pattern analysis, two temperature conditions with clear differences in the response of the MOS sensor to the odorous substances were identified to compare and examine whether it is possible to identify the odorous substances by a single MOS sensor using a two-dimensional (2D) pattern analysis where the two temperature conditions compose the x-axis and the y-axis, respectively. Finally, this study suggests a simple method of pattern analysis with the 2D x-y coordinates to identify the odorous substances without using a complicated algorithm such as a neural network.

2. EXPERIMENTAL

This study was conducted to examine the difference in response to hydrogen sulfide and toluene gases by controlling the temperature of a semiconductor gas sensor. For the semiconductor gas sensor, the commercial TGS2602 model of FIGARO, Japan, was applied. The rated voltage required for the TGS2602 sensor’s heater is 5 V, this study applied the temperature transient method to reduce the voltage of the heater in 0.5 V steps from 5 V to vary the sensor temperature.

The experimental system was configured as shown in Fig. 1 and the sensor was installed on the 3 l batch-type response system to inject diluted hydrogen sulfide, ammonia, or toluene gas using a syringe to set the concentration at 0~50 ppm. The output voltage (Vout) from the sensor was saved onto the data logger to analyze the signals. The voltage of the heater applied to the TGS2602 sensor was reduced by 0.5 V every 30 s using a DC power supply to measure the response to odorous substances by voltage.

The voltage response from the sensor was measured 1 s to be saved onto the data logger (Graphtec G220 model) or monitored on a PC in real-time and the sensor’s Vout and resistance (Rs) were derived to compare the characteristics of the hydrogen sulfide, ammonia, and toluene gases. In addition, Ro was set as the sensor resistance in the odorless air condition in the process of deriving the sensitivity of the sensor (Rs/Ro).

The characteristics of the odorous substances according to the temperature of the semiconductor gas sensor can be derived using 2D(x-y coordinates) characteristic curves; the 2D x-y coordinates were derived by setting the x-axis as the sensor response in the normal sensor temperature condition and the y-axis as the sensor response in a low-temperature condition of the sensor with the same concentration.
3. RESULTS AND DISCUSSIONS

3.1 Response characteristics of sensor by temperature

Fig. 2 shows the response characteristics of the MOS sensor to hydrogen sulfide according to the temperature conditions. Fig. 2(a) shows the response characteristics when the voltage to the sensor heater was decreased by 0.5 V in the odorless air condition, and Fig. 2(b) shows the response characteristics with 5 ppm hydrogen sulfide gas. In the odorless air condition, the sensor response decreases in proportion to the sensor temperature, but the response of the MOS sensor to the hydrogen sulfide gas increased as the response increased in approximately 2.5 min (with 2.5 V).

Lantto et al. [11] also showed that the SnO$_2$ sensor’s sensitivity to hydrogen sulfide gas was highest at approximately 150°C, which was lower than the normal temperature of 400°C and suggested a way to improve the selectivity to hydrogen sulfide gas using a cooling process to resolve the weakness of the MOS sensor. In addition, Lee et al. [12] showed that the sensor sensitivity decreased when the sensor’s temperature was raised from 250°C to 450°C, and the temperature that secured the highest sensitivity of the SnO$_2$-based MOS sensor to hydrogen sulfide was a low temperature of approximately 200°C.

In addition, when the same MOS sensor’s response signal circuit resistance ($R_L$) was changed to 4.4, 8.2, 12.0, or 15.1 kΩ, the sensor’s temperature profile for hydrogen sulfide gas increased in proportion to the resistance, but the response drew an acclivity again from 2.5 V of sensor heater voltage, which was approximately 2.5 min later.

Fig. 2(c) and Fig. 2(d) shows the response profile of the MOS sensor to ammonia and toluene gases according to the temperature of its heater. As with the test of hydrogen sulfide gas, the sensor’s response decreased proportionately when the sensor’s heater temperature was reduced by 0.5 V from 5.0 V every 30 s through cooling. This was completely different from the response characteristics for hydrogen sulfide gas; when the temperature of the MOS sensor’s heater was high, the responses of ammonia and toluene gases were high, whereas the response of hydrogen sulfide gas was high when the heater’s temperature was low.

In addition, the response profile tended to decrease
proportionately with the MOS sensor sensitivity when the temperature conditions of the ammonia and toluene gases changed, but the sensitivity change of the MOS sensor to the ammonia gas was relatively large in the high-temperatures range of 5.0 to 4.0 V. The toluene gas showed a gradual decrease in MOS sensor sensitivity throughout the temperature range, making it possible to see minor differences in the response characteristics for the ammonia and toluene gases according to the change in the MOS sensor's temperature conditions.

The response profile of toluene gas according to the temperature of the MOS sensor's heater showed a similar tendency to the results for air, methane (CH\textsubscript{4}), and ethane (C\textsubscript{2}H\textsubscript{6}) gases reported by Nakata et al. [13,14], and the response increased when the sensor's temperature was approximately 350°C compared to about 210°C. The difference in response profile according to the odorous substances showed the same tendency even when the sensor response's resistance (R\textsubscript{s}) changed, manifesting that the sensor surface's physical/chemical characteristics change according to the sensor temperature.

In order to examine the sensitivity of the MOS sensor according to the odorous substances, the sensor's sensitivity (Rs/Ro) was calculated using the sensor's response profile according to the heater's temperature change. Here, Ro was set as the sensor's response to odorless air at the initial temperature of 5.0 V, and Rs was set as the sensor's response according to its heater's temperature for the odorous substances. Fig. 3 shows the ratio of Rs to Ro. Fig. 3(a) shows the sensor's sensitivity to hydrogen sulfide gas; the sensitivity is approximately 1.0 in the odorless air condition, and the sensor's sensitivity falls below 1.0 when the MOS sensor's sensitivity to hydrogen sulfide gas increases.

When the heater's voltage was cooled from 5.0 V to 4.5 V, the sensor's sensitivity (Rs/Ro) also decreased; when cooled below 4.0 V, the sensor's sensitivity (Rs/Ro) increased gradually and then sharply at 2.5 V.

On the other hand, although there was a difference in the decrease in temperature, the sensor's sensitivity (Rs/Ro) to the ammonia and toluene gases in Fig. 3(b) and Fig. 3(c) was at a peak compared to odorless air at 5.0 V, and gradually decreased as the heater cooled. The difference in the sensor's sensitivity pattern according to the odorous substance could be suggested as a new way to improve the selectivity to odorous substances simply by changing the sensor temperature.

Morrison et al. [15] and Sears et al. [16] assumed that the MOS sensor’s dependence on temperature is caused by variation with temperature in the stability of adsorbed oxygen species (O\textsuperscript{2}-, O\textsuperscript{-}, O\textsuperscript{2-}) on the sensor surface, but it is actually caused by the optimum oxidation (response) temperature characteristics according to the type of odorous substance, and manifests that there are various factors that affect the sensor, such as the sensor's sensing matter and catalysts.
3.2 Response characteristics according to the concentration of odorous substances

Fig. 4 shows the sensitivity profile of the odorous substances hydrogen sulfide, ammonia, and toluene gases by concentration according to the temperature of the MOS sensor. Fig. 4(a) shows the cases of hydrogen sulfide gas concentration at 5, 10, and 15 ppm; the response also increased from 2.5 V when the sensor’s heater was cooled. In addition, the response characteristics of the MOS sensor were clearly exhibited by cooling in low concentrations below 5 ppm. In high concentrations, the sensor heater’s cooling did not have much impact on the response characteristics. It was concluded that the MOS sensor’s response to high-concentration hydrogen sulfide gas was high to minimize the impact of temperature.

In the same manner, Fig. 4(b) shows the sensitivity profile of the MOS sensor according to the concentration of ammonia and toluene gases. The concentrations of ammonia and toluene gases were controlled from 5~50 ppm; the sensitivity varied by concentration, but it was highest when the MOS sensor’s heater was set at 5.0 V. The sensor’s sensitivity (Rs/Ro) was greater than 1.0 because the Rs value for the ammonia and toluene gases in the low-temperature range of the sensor became greater than the Ro value for odorless air. As Rs increased to a relatively large value, it was meaningless to calculate the sensitivity of the sensor.

As a result of varying the concentration of hydrogen sulfide, ammonia and toluene gases, the response characteristics showed similar tendencies to the temperature of the MOS sensor and the difference in the response of odorous substances according to the temperature of the MOS sensor can be understood as the unique response characteristics of odorous substances and the MOS sensor.

The difference in odorous substances’ sensitivity profiles according to the temperature of the MOS sensor can be understood as a unique response pattern for odorous substances. A single MOS sensor was used to identify the difference in the response characteristics for the major odorous substances of hydrogen sulfide, ammonia and toluene gases, and it was necessary to introduce a way to express the pattern characteristics of these odorous substances by objective values.

3.3 Pattern analysis for the classification of odorous substances

It was verified that it is possible to classify the odorous substances of hydrogen sulfide gas and toluene gas based on the sensitivity profile according to the temperature of the MOS sensor. As in the study of Moon et al. [17], a radar chart pattern was used to derive from the sensitivity profile the visual patterns to classify the types of odorous substances.

Fig. 5 shows the radar chart pattern of the sensor’s response
response to hydrogen sulfide gas is opposite to its response to other odorous substances (ammonia and toluene). In addition, the ammonia and toluene gases, which showed a subtle difference in response (Rs) according to the MOS sensor's temperature, showed different pattern characteristics.

The types of odorous substances can be classified using pattern analysis on the response characteristics of the MOS sensor according to temperature, but it is difficult to configure and run the system for the analysis because visualizing the pattern characteristics through PCA requires a complicated statistical tool [7,18].

The pattern characteristics according to each odorous substance's concentration also showed clear linearity for the hydrogen sulfide and ammonia gases, and the response of the MOS sensor did not show much difference for toluene gas over 10 ppm concentration with low linearity. It would be possible to quantify the MOS sensor used in this study up to 15~20 ppm concentration for the hydrogen sulfide and ammonia gases and up to 10 ppm for the toluene gas because of its relatively high response.

This study suggests a characteristic curve to easily classify the odorous substances using a 2D x-y pattern analysis. The 2D x-y pattern analysis identified the MOS sensor’s temperature as the factor that can clearly classify the hydrogen sulfide, ammonia, and toluene gases. This study conducted an (x, y) coordinate pattern analysis with the MOS sensor’s temperature that responds to the ammonia and toluene gases in the x-axis and the temperature that responds to the hydrogen sulfide gas as the y-axis. As a result, it generated coordinate data to set the temperature of the MOS sensor at 5.0 V as the x-axis and the temperature at 2.5 V as the y-axis.
Fig. 7 shows the results of the x-y pattern coordinates for the hydrogen sulfide, ammonia, and toluene gases. It was possible to acquire specific x-y coordinates for each odorous substance and draw a characteristic curve with a certain straight line for the x-y coordinates according to the concentration of each odorous substance. The hydrogen sulfide gas was clearly identified by a curve with a slope of 1.73, the ammonia gas with a slope of 0.05, and the toluene gas with a slope of 0.52.

Therefore, a simple 2D x-y pattern analysis was conducted to classify the odorous substances using two different MOS sensor temperature conditions; the analysis showed clearly different responses to the odorous substances. This method of pattern analysis is relatively simple compared to the existing PCA and ANN to identify the odorous substances more easily, and is considered a highly attractive method of pattern analysis because it is possible to identify a unique characteristic curve for each odorous substance.

4. CONCLUSIONS

As a way to improve the selectivity of a MOS sensor, a study was conducted to identify the types of odorous substances with the changes in the pattern of response signals by gradually reducing the sensor temperature. When the single MOS sensor’s voltage was gradually reduced by 0.5 V from 5.0 V to cool the sensor, the sensor’s sensitivity was highest at approximately 2.5 V for the hydrogen sulfide (H2S) gas and at approximately 5.0 V for the ammonia (NH3) and toluene (C6H5CH3) gases.

In addition, a 2D x-y pattern analysis using the sensor temperature condition that yields the highest sensitivity to each odorous substance identified each odorous substance with characteristic curves. The hydrogen sulfide gas drew a characteristic curve with the slope of 1.73, whereas the ammonia gas drew a slope of 0.05 and the toluene gas drew a slope of 0.52. This method of 2D x-y pattern analysis could easily classify the odorous substances without using complicated methods of statistical analysis and could be applied in various ways in the future.

An electric nose array system with m temperature conditions applied to n MOS sensors could secure a wide range of pattern data as many as n × m considering the temperature conditions whereas the previous systems could only acquire data limited to the size of n. Therefore, varying the temperature conditions of the MOS sensor could be as effective as developing new MOS sensors.

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