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Batch-processed semiconductor gas sensor array for the selective detection of NO_x in automotive exhaust gas

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Abstract

This paper reports on a semiconductor gas sensor array to detect nitrogen oxides (NO_x) in automotive exhaust gas. The proposed semiconductor gas sensor array consisted of one common electrode and three individual electrodes to minimize the size of the sensor array, and three sensing layers [TiO_2 + SnO_2 (15 wt%), SnO_2, and Ga_2O_3] were deposited using screen printing. In addition, sensing materials were sintered under the same conditions in order to take advantage of batch processing. The sensing properties of the proposed sensor array were verified by experimental measurements, and the selectivity improved by using pattern recognition.

Keywords: Nitrogen oxides (NO_x), Semiconductor gas sensor array, Common electrode, Batch processing, Pattern recognition

Background

Semiconductor gas sensors are utilized in the detection of oxidizing and reducing gases by measuring the conductance changes caused by chemical adsorption of gases on metal oxide semiconductor surfaces. However, employing semiconductor gas sensors is inappropriate for automotive diesel engines because most metal-oxide-based gas sensors, such as WO_3 and CuO, operate at low temperatures range between 100 and 300 °C [1, 2]. Although SnO_2, TiO_2, Ga_2O_3, and In_2O_3 are widely used as high-temperature (500–600 °C) gas sensor materials, the lack of gas selectivity is a major drawback of semiconductor gas sensors. Because the oxidizing (NO_2) and reducing (CO) gases have similar chemical characteristics that tend to react with the electron and ionosorbed oxygen species, respectively. The gas selectivity of metal-oxide-based gas sensors can be improved by adding other metal oxides or dopants (Pt, Pd, Al, Cr, etc.) [3–6]. Following previous literatures, adding other metal oxides and dopants plays an important for promoting the specific gas sensing reaction by the spilled over effect [7, 8]. These studies improved the gas selectivity, but the lack of gas selectivity has not been perfectly resolved.

On the other hand, there have been several reports on semiconductor gas sensor arrays. The implementation of a sensor array that consists of various metal-oxide sensing layers combined with pattern recognition is one of the methods that compensate this drawback. K. Persaud and G.H. Dodd first presented a report on a sensor array in 1982 [7]. After that, many research teams conducted studies on sensor arrays for the detection of gases in various fields such as environmental monitoring, food and beverage analysis, and disease diagnosis [8–10]. However, it is difficult to reduce the distance between the sensing layers of a sensor array because the metal oxides have different operating temperatures. In addition, it is difficult to conduct batch processing because processing conditions are different for each sensing material.

Therefore, in this paper, a new design for a gas sensor array that is advantageous to miniaturization and batch processing is proposed. SnO_2-doped TiO_2, SnO_2, and Ga_2O_3 were used as the materials of the sensing layers. The sensing layers were deposited on an Al_2O_3 wafer by screen printing. As these three sensing layers operate at the same temperature, so the proposed gas sensor array does not need to be concerned about the thermal

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interference by a micro-heater. For this reason, distance between the sensing layers is not a major consideration, and the sensor array can use a proposed common electrode in this paper. In addition, the three deposited sensing layers were sintered at the same temperature (1100 °C). The gas-sensing properties of the fabricated gas sensor array were evaluated by detecting NO_2, CO, and NO gases at high temperature (600 °C). The selectivity of the array was improved through a pattern recognition program.

Findings

Design and fabrication

The proposed design that is advantageous to miniaturization of the gas sensor array is shown in Fig. 1. The gas sensor array was fabricated on an Al_2O_3 substrate. The interdigitated (IDT) platinum electrode, consisting of a common electrode and three individual electrodes that are interdigitated, was deposited on an alumina substrate by using an e-beam evaporator. Then, SnO_2 (15 wt%)-doped TiO_2, SnO_2, and Ga_2O_3 printable paste was deposited on the IDT electrode using screen printing. The sensing layer thickness was 1.5–2 µm. The proposed gas sensor array needs only one micro-heater because the three materials of the sensing layers can detect oxidizing and reducing gases at the same temperature (600 °C). Although gas testing was performed using a tube furnace, a micro-heater will be integrated in the future. The entire substrate size is 1.5 cm^2, the sensing layers size is 2.5 mm (width) × 4.5 mm (length), and the distance between the sensing layers is 100 µm. The sensor array is also advantageous to use batch processing because TiO_2, SnO_2, and Ga_2O_3 can be sintered at the same temperature (1100 °C for 2 h).

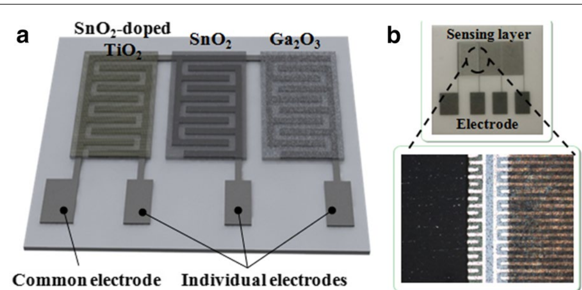

Fig. 1 **a** Proposed design of semiconductor gas sensor array, and **b** fabricated semiconductor gas sensor array

Experimental details

Figure 2 shows a block diagram of the apparatus for gas testing. The experimental setup included a test section, a gas flow system, data acquisition, and a ventilation system. The sensing properties of the sensor array were evaluated inside the quartz pipe. N_2 was used as a null gas, and typical emissions (NO_2, CO, and NO) were used as target gases. The operating temperature was fixed at 600 °C using a tube furnace, and the gas flow rate was also fixed at 1 l/min using a mass flow controller (MFC). The resistances of the sensor array were measured using an I-V source meter. Measurements of the gas sensor array responses were conducted upon its exposure to various concentrations of individual gases or mixtures of gases in order to accumulate the sensor array data for pattern recognition.

Results and discussion

Figure 3 shows the sensitivities of NO_2, CO, and NO (200 ppm) detection at 600 °C. The sensitivity of the gases was defined as $(R_{null} - R_{gas})/R_{gas}$, where R_{null} and R_{gas} were resistance in null (N_2) gas and in the target gases (NO_2, CO, and NO), respectively. All sensing layers exhibited the highest sensitivity to NO_2, as shown in Fig. 3. However, the highest sensitivity (3.6) to NO_2 was obtained for the TiO_2-based sensing layer, and the highest sensitivity (−0.611 and 0.625) to CO and NO was obtained for the SnO_2 and Ga_2O_3 sensing layers, respectively.

In order to verify the reliability of the sensor array, the experiments were performed in the presence of various NO_2, CO, and NO concentrations at 600 °C. The results of the gas concentration tests are shown in Fig. 4. The response times (T33–T66) were 10.4–20.5 s. As shown in Fig. 4, the responses of the sensors are proportional to the concentration of gases. Moreover, the Ga_2O_3 sensing layer did not respond to CO at low concentrations, i.e., below 100 ppm.

Table 1 shows the relative responses of the sensor array upon exposure to various concentrations of target gases. The relative response was defined as the relative sensitivity to target gases at 200 ppm. All sensing layers exhibited unique response patterns according to the gases.

However, despite the unique response pattern, quantitatively measuring concentrations of gases is difficult for a mixture of gases. Employing artificial neural networks (ANNs) is effective in identifying the types and

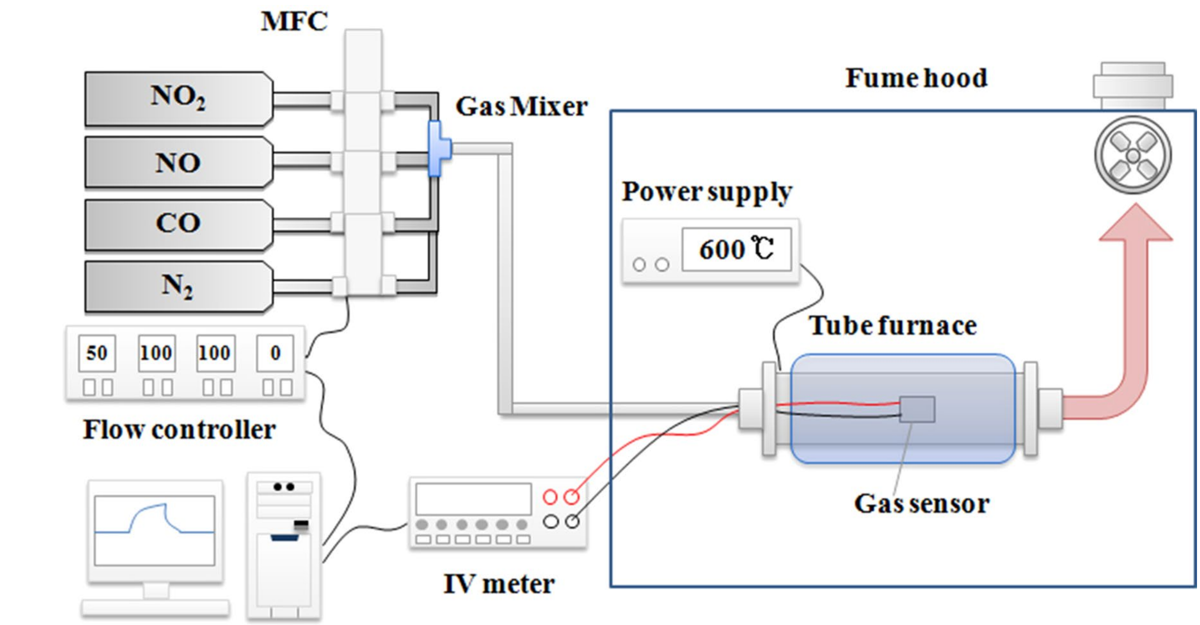

Fig. 2 Schematic diagram of experimental setup for measuring concentrations of gases

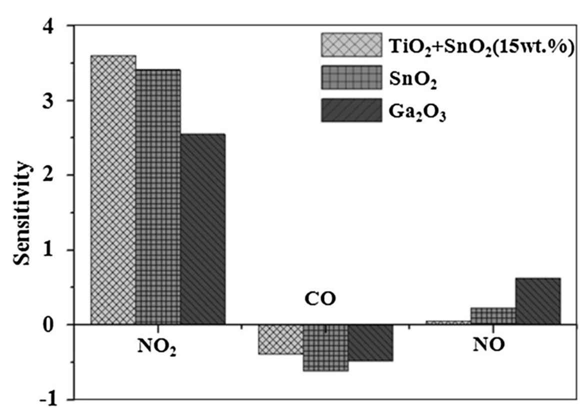

Fig. 3 Sensitivity of gas sensor array. SnO_2-doped TiO_2, SnO_2, and Ga_2O_3 sensing layers exhibit p-type behavior to target gases at 600 °C

some concentrations of the chemical species. ANNs is a model created by imitating the information processing of the brain, and it is achieved by learning data. A back-propagation (BP) algorithm is a common method of learning ANNs. The BP algorithm requires known output values for each input value to the learning ANNs. BP algorithm consists of an input layer, hidden layer, and output layer, as shown in Fig. 5. The input values are calculated with weight using a linear combination in the hidden layer, and the calculations use an activation function. A sigmoid function is commonly used as the activation function. Weights are optimized at each node until the error between the calculations and the known output values is minimized, and then the training is stopped.

A NeuroXL Predictor was used to train the experimental data in Table 1. A sigmoid function was used as an activation function; the initial weight was set to 0.3. After adjusting the weights 15,000 times, training was completed. To predict non-learning data, an additional experiment was performed using the concentrations of NO_2, CO, and NO emitted during actual vehicle driving conditions [11]. Table 2 shows the additional experimental conditions and the results of the sensor array. The concentrations of gases were predicted as shown in Fig. 6. The errors of the predicted values were, respectively, −12.6, −19.0, and −19.8 % for NO_2, CO, and NO, as shown in Fig. 6.

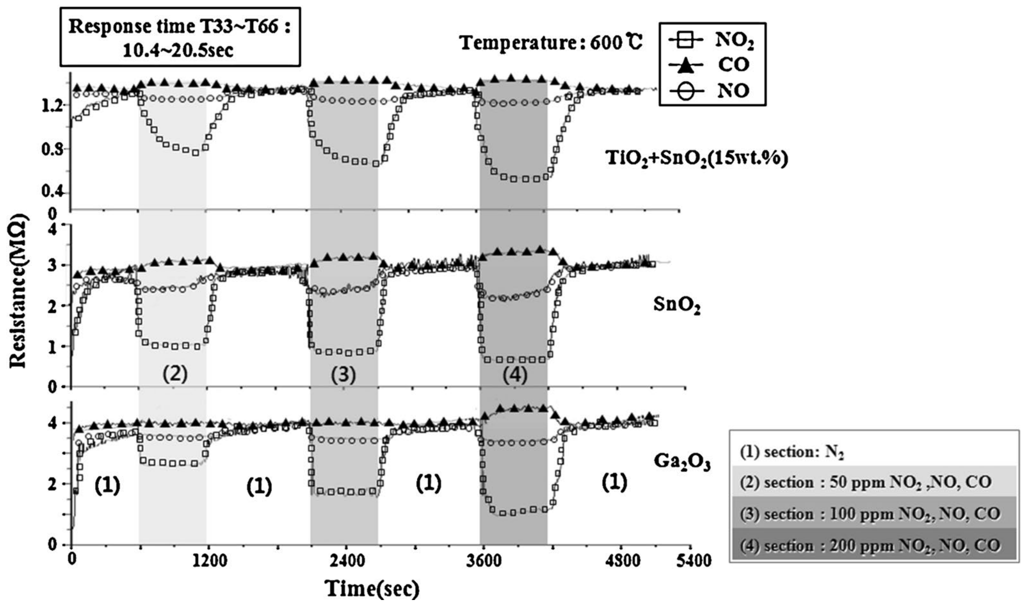

Fig. 4 Measured resistance of gas sensor array (SnO_2-doped TiO_2, SnO_2, and Ga_2O_3) upon exposure to various concentrations of NO_2, CO, and NO with bias voltage of 2 V

Table 1 Relative response of gas sensor array

Concentration (ppm)			Relative response (ΔR/R)		
NO_2	CO	NO	SnO_2-doped TiO_2	SnO_2	Ga_2O_3
Individual gas					
50	0	0	1.99	2	0.792
100	0	0	2.5	2.46	1.81
200	0	0	3.6	3.41	2.55
0	50	0	−0.308	−0.454	0
0	100	0	−0.373	−0.503	0
0	200	0	−0.388	−0.611	−0.485
0	0	50	0.04	0.1	0.47
0	0	100	0.045	0.17	0.525
0	0	200	0.053	0.23	0.625
0	0	500	0.278	1.22	1.4
Mixture of gases					
200	200	0	3	2.78	2.54
200	0	200	3.21	3.82	2.83
0	200	200	0.327	0.371	0.404
200	200	100	1.67	3	2.45
200	100	200	1.59	2.87	2.63
100	200	200	1.4	1.63	1.63
200	200	200	1.53	2.69	2.03
50	50	50	1.22	0.477	0.887
100	50	50	1.32	0.85	1.47
200	50	50	1.59	1.27	2.27
50	100	100	0.956	0.512	0.845
100	100	100	1.29	0.974	1.29
200	100	100	1.89	1.92	2.06

Results of gas sensor array upon exposure to various concentrations of individual gas and mixture of gases

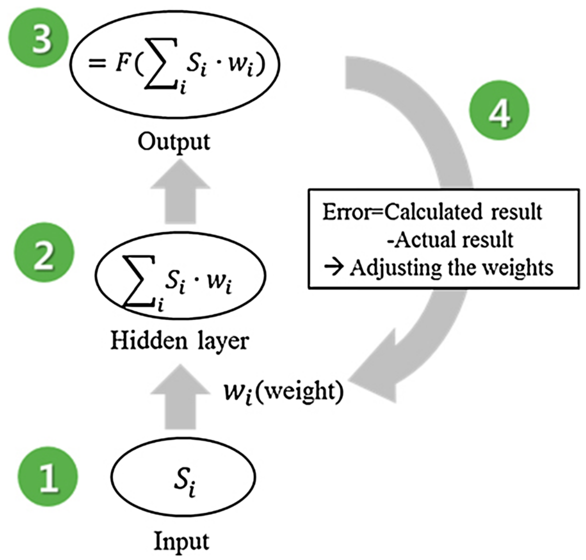

Fig. 5 Training process of BP algorithm

Table 2 Experimental conditions and results of gas sensor array

	NO_2	CO	NO
Experimental conditions			
Concentration (ppm)	40	123	160
Sensing layer	**SnO_2-doped TiO_2**	**SnO_2**	**Ga_2O_3**
Results			
Relative response (ΔR/R)	0.951	0.5	0.834

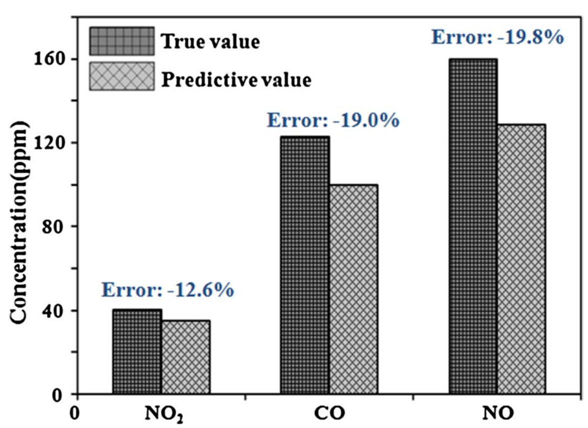

Fig. 6 Results of pattern recognition

Conclusions

A proposed gas sensor array was fabricated by using the MEMS technique. The sensor array consists of one common electrode and three individual electrodes. The gas sensor array has three sensing layers; SnO_2 (15 wt%)-doped TiO_2, SnO_2, and Ga_2O_3. The three sensing layers were deposited on an IDT platinum electrode and were successfully sintered at 1100 °C for 2 h. Overall the gas sensor array size is 1.5 cm^2 and the distance between the sensing layers is 100 µm. Although the other literatures did not precisely specify the distance between the sensing layers, their sizes were in the range of about 0.5–1 mm [14–16]. Proposed design of gas sensor array will contribute to miniaturizing the sensor array. The fabricated gas sensor array shows a unique response pattern according to NO_2, CO, and NO at 600 °C. The NeuroXL Predictor was used to identify NO_2, CO, and NO among a mixture of gases. By a −12.6 to −19.8 % error, non-learning gas data could be predicted using an artificial neural networks. Although there were some errors, the feasibility of the proposed gas sensor array to recognize a mixture of gases has been demonstrated. If additional gas data is acquired, it is expected that the error will be reduced.

Authors' contributions

YJK conceived the idea and supervised the project. YJK and HJJ discussed the design and the fabrication process of the gas sensor array. HJJ and MKK performed the experimental measurements and analysis of the results. YJK and HJJ drafted the manuscript. All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

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