Fabrication and characterization of a small-sized gas identification instrument for detecting LPG/LNG and CO gases

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Abstract—A small-sized gas identification system has been fabricated and characterized using an integrated gas sensor array and artificial neural-network. The sensor array consists of four thick-film oxide semiconductor gas sensors whose sensing layers are In_2O_3-Sb_2O_5-Pd-doped SnO_2 + Pd-coated layer, La_2O_5-$PdCl_2$-doped SnO_2, WO_3-doped SnO_2 + Pt-coated layer and ThO_2-V_2O_5-$PdCl_2$-doped SnO_2. The small-sized gas identification instrument is composed of a GMS 81504 containing an internal ROM (4k bytes), a RAM (128 bytes) and four-channel AD converter as MPU, LEDs for displaying alarm conditions for three gases (liquefied petroleum gas: LPG, liquefied natural gas: LNG and carbon monoxide: CO) and interface circuits for them. The instrument has been used to identify alarm conditions for three gases among the real circumstances and the identification has been successfully demonstrated.

Index Terms—Thick-film oxide semiconductor gas sensor, Gas sensor array, Artificial neural network, Gas/odor identification

I. INTRODUCTION

During the last few years, the term 'gas/odor identification' has been widely used. A gas/odor identification system is a tool designed for mimicking human olfactory system. It comprises of a gas sensor array corresponding to olfactory receptors of human nose and an appropriate pattern-recognition system, capable of recognizing simple or complex odors [1-3]. Considerable attempts to develop the gas identification system have been made for applications in the fields of foods, drinks, cosmetics, environmental monitoring, etc. [4-8]. There are several gas identification instruments commercially available at present and they are generally large, bulky, expensive and somewhat difficult to operate. They also require PC for control and signal processing. However, there are many application areas where a small, portable instrument would be desirable like monitoring of toxic gases in closed environments and monitoring of food quality such as freshness, flavor, fermentation, etc.

Development of a small, portable gas identification instrument, therefore, has become a demanding requirement because of its advantages such as small size, low cost and easy manipulation in comparison with the ordinary gas identification instrument.

The objective of this work is to identify alarm conditions for LPG/LNG and CO gases among the real circumstances by a small-sized gas identification instrument using an integrated gas sensor array whose sensing layers are In_2O_3-Sb_2O_5-Pd-doped SnO_2 + Pd-coated layer, La_2O_5-$PdCl_2$-doped SnO_2, WO_3-doped SnO_2 + Pt-coated layer and ThO_2-V_2O_5-$PdCl_2$-doped SnO_2 along with pattern-recognition techniques such as principal component analysis and back-propagation artificial neural-network.

II. EXPERIMENTAL

Fig. 1 presents the schematic view of an integrated gas sensor array formed on an alumina substrate by a screen printing method. The integrated sensor array consists of such thick-film oxide semiconductor sensing materials as In_2O_3-Sb_2O_5-Pd-doped SnO_2 + Pd-coated layer (S1), La_2O_5-$PdCl_2$-doped SnO_2 (S2), WO_3-doped SnO_2 + Pt-coated layer (S3) and ThO_2-V_2O_5-$PdCl_2$-doped SnO_2 (S4).

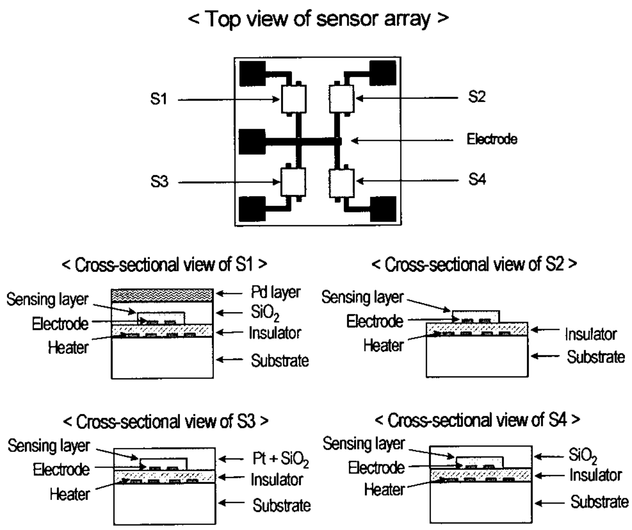

Fig. 1. Schematic view of the thick-film oxide semiconductor gas sensor array.

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The processing steps are indicated in Fig. 2. Four different pastes were prepared by mixing sensing materials with organic vehicle using three-roll mill and they are respectively printed on the Pt electrodes to form the sensing layers. The pure SiO_2 layer or SiO_2 layers containing Pt or Pd were obtained on the sensing layers by several repetition of a droplet dropping of a pure SiO_2 sol solution or SiO_2 sol solution containing noble metals such as Pt and Pd. Conditions for the fabrication of the four sensors are shown in Table 1. S1 was designed for detecting hydrocarbon gases such as CH_4, C_3H_8, C_4H_{10}, etc. The sensing material for S1 was obtained through coprecipitation process. The details of the sensing material characteristics have been described elsewhere [9-10]. S2 was prepared for selective detecting solvent species like ethanol. S3 was fabricated for detecting various reducing gases with high sensitivity. S4 was used as a dummy sample.

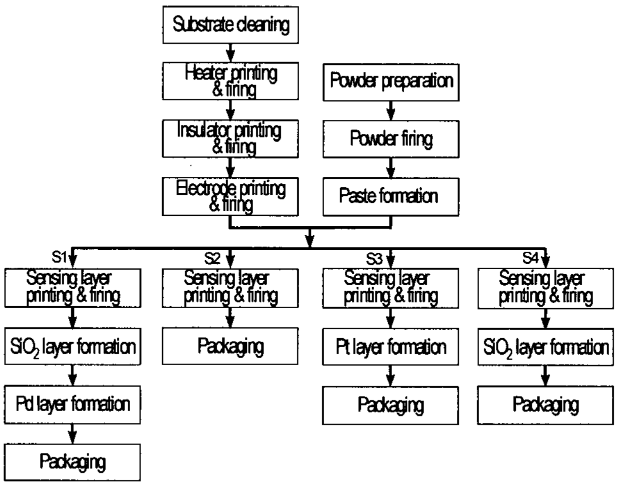


Fig. 2. Processing steps of the thick-film gas sensor array.

Table 1. Conditions for the fabrication of the sensor

	Sensing materials	Powder firing temp	Sensing layer firing temp	Operating temp
S1	(SnO_2 : In_2O_3 : Sb_2O_5 : Pd = 84 : 10 : 5 : 1 wt.%) + Pd-coated SiO_2 layer	600℃	700℃	400℃
S2	SnO_2 : La_2O_5 : $PdCl_2$ = 94.5 : 5 : 0.5 wt.%	600℃	700℃	400℃
S3	(SnO_2 : WO_3 = 95 : 5wt.%) + Pt-coated SiO_2 layer	600℃	700℃	400℃
S4	(SnO_2 : ThO_2 : V_2O_5 : $PdCl_2$ = 94 : 1.5 : 3 : 1.5 wt.%) + SiO_2 layer	600℃	700℃	400℃

The measurement of the gas sensing properties was carried out in a system fully controlled by a PC as shown in Fig. 3. The gas measurement system is composed of a CPU, a ROM for storing system main program, an EEPROM for containing operation conditions of the sensors, AD and DA converters for signal processing of the sensors, and a notebook PC. The notebook PC was used to read out the sensor outputs through RS232 communication, to train the optimum connection weights among input, middle and output layers of back-propagation artificial neural-network.

The small-sized gas identification system for the confirmation of LPG/LNG and CO gases is presented in Fig. 4. The system consists of a GMS 81504 containing an internal ROM, a RAM and four-channel AD converter as MPU, three LEDs for displaying alarm conditions for three gases and interface circuits for them. Once the optimized connection weights of the network obtained from the gas measurement system are stored in the internal ROM of the gas identification instrument through a ROM writer, the system can identify alarm conditions for three gases.

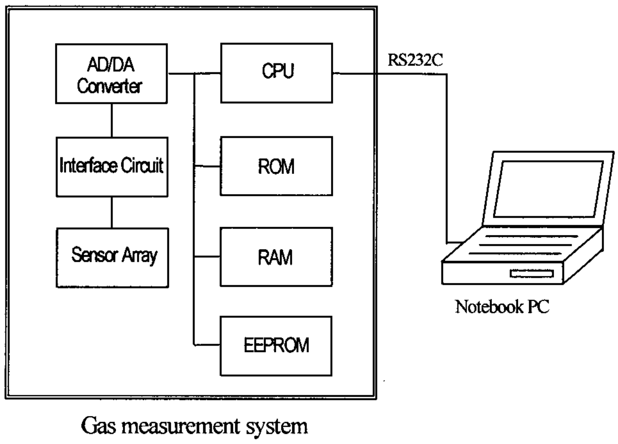


Fig. 3. Schematic diagram of the gas measurement system.

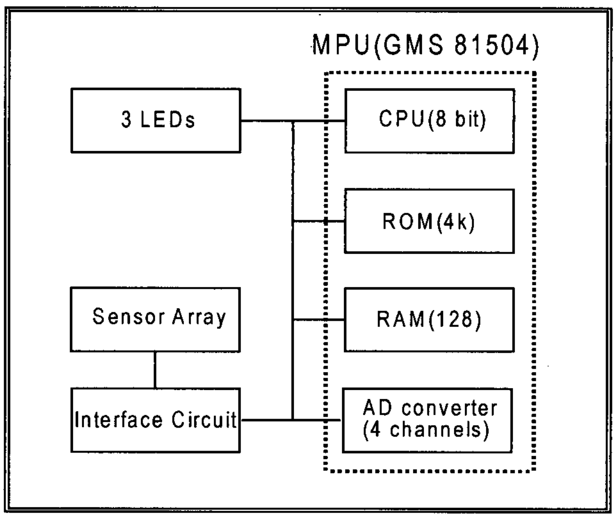
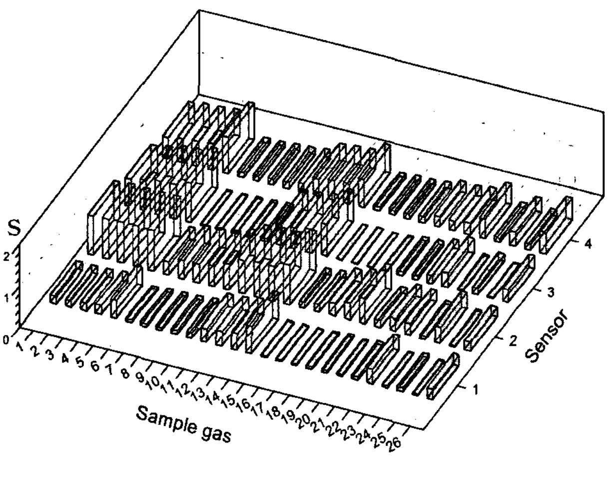


Fig. 4. Schematic diagram of the gas identification instrument.

III. RESULT AND DISCUSSION

Fig. 5 shows the sensitivity of the integrated gas sensor array for 26 gas samples at the operating temperature of 400℃. The sensitivity (S) was defined as R_{gas}/R_{air}, where R_{air} and R_{gas} are the resistance of the sensor in air and upon exposure to the gas to be measured, respectively. The sensitivity accordingly decreases below unity as the gas concentration increases. Upon exposure to target gases, the sensors exhibited resistance changes and the sensitivity strongly depended on the sensing layer materials. S1 and S2 showed better sensitivity than any other sensors for CH_4 and C_2H_5OH, respectively. S3 displayed high sensitivity for reducing gases such as C_4H_{10}, C_2H_5OH and H_2 gases. The sensors were also exposed to various smells such as Korean spices and condiments (garlic, onion, soy, soybean paste and fermented soybeans), Korean style roast fish and roast beef, Korean hot noodle, tobacco smoke, etc. for real applications of LPG/LNG and CO detector. The sensors were very sensitive to these strong smells. The sensitivities of four trials for each target gas as shown in Fig. 5 were used as input parameters for principal component analysis.



Gas 1 : CH_4 2.5%	10 : C_4H_{10} 0.05%	19 : H_2 0.04%
2 : CH_4 1.25%	11 : CO 400ppm	20 : C_2H_5OH 0.1%
3 : CH_4 1.0%	12 : CO 300ppm	21 : Soybean paste
4 : CH_4 0.8%	13 : CO 200ppm	22 : Roast fish (mackerel)
5 : CH_4 0.05%	14 : CO 50ppm	23 : Roast beef
6 : C_4H_{10} 0.9%	15 : H_2 2.0%	24 : Hot noodle
7 : C_4H_{10} 0.45%	16 : H_2 1.0%	25 : Garlic+onion+soy+ fermented soybeans
8 : C_4H_{10} 0.3%	17 : H_2 0.4%	26 : Tobacco smoke
9 : C_4H_{10} 0.2%	18 : H_2 0.2%	

Fig. 5. Sensitivity of the gas sensor array for 26 gas samples.

Since CO is very dangerous even below 200 ppm warning is needed around that concentration region. Table 2 indicates test conditions for LPG/LNG gas detector based on KOFEIS (Korea Fire Equipment Inspection Standard). The small gas identification instrument was designed for LPG/LNG and CO gases to alarm by above-mentioned conditions. Fig. 6 exhibits the result of principal component analysis for 26 gas samples. Data patterns were separated by three groups: LPG/LNG alarm, CO alarm and No alarm. Data patterns are not overlapped among the groups and the pattern separation is very sharp. The result suggests that it is promising to discriminate the groups using neural-network analysis.

Table 2. Test conditions for LPG/LNG gas detector

Detection Gases	Test Gases	Test Concentration(%) for 'alarm' signal	Test Concentration(%) for 'no alarm' signal
LPG	C_4H_{10}	0.45	0.05
LNG	C_4H_{10} H_2 CH_4	0.45 1.00 1.25	0.05 0.04 0.05

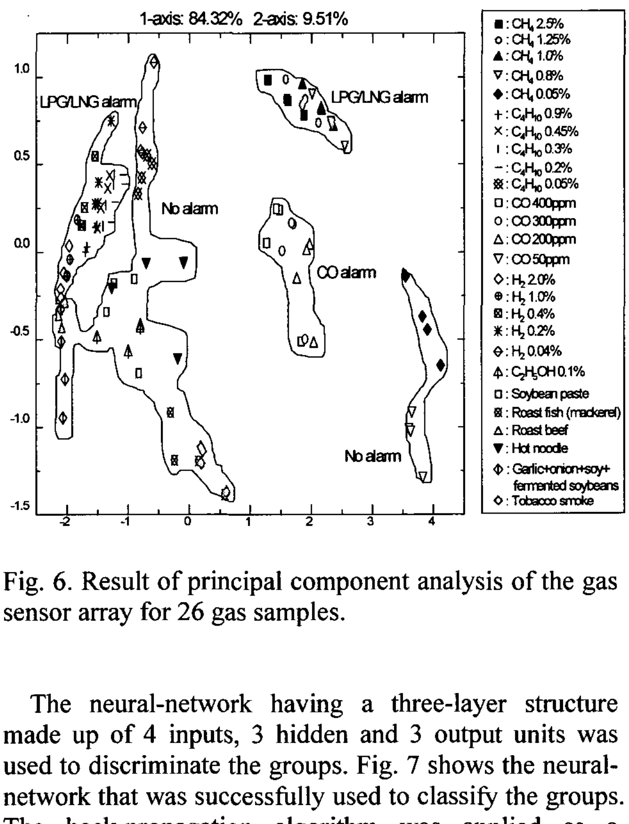


Fig. 6. Result of principal component analysis of the gas sensor array for 26 gas samples.

The neural-network having a three-layer structure made up of 4 inputs, 3 hidden and 3 output units was used to discriminate the groups. Fig. 7 shows the neural-network that was successfully used to classify the groups. The back-propagation algorithm was applied as a supervised learning rule. The signals of the four sensors were used as the input layer. Three groups were used as the output layer. The network was trained using data so that the desired outputs could be obtained. The connections between hidden and both input and output layers were optimized after 5000 times training for our gas samples. The recognition probability of the neural-network analysis, defined as the ratio of number of right answers to that of total trials was 100% for each four trials of three sample groups. This result clearly shows that the small-sized gas identification instrument can be effectively used as a leakage alarm device for LPG/LNG and CO gases. Photograph of the instrument is shown in Fig. 8. (12cm x 18cm x 3.5cm)

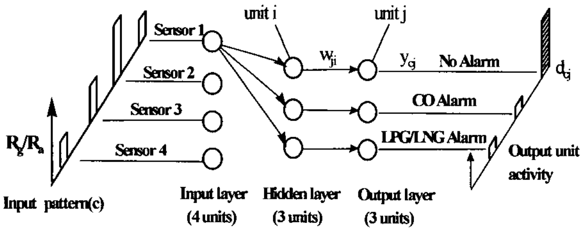


Fig. 7. Three-layer structure of the neural network.

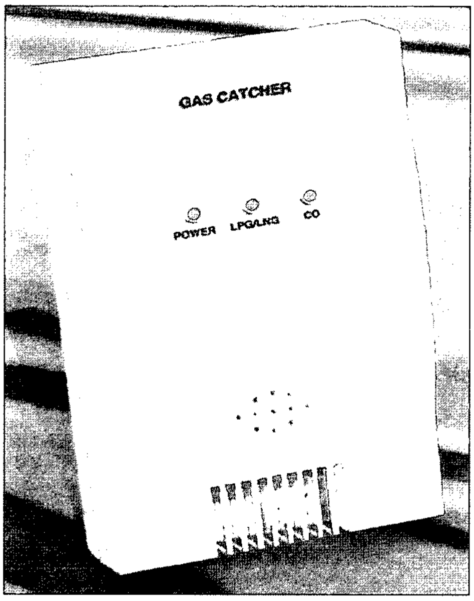


Fig. 8. Photograph of the small-sized gas identification instrument.

IV. CONCLUSION

A small-sized gas identification system has been fabricated and characterized using an integrated gas sensor array and pattern-recognition techniques such as principal component analysis and back-propagation artificial neural-network. The sensor array consists of such thick-film oxide semiconductor gas sensing materials as In_2O_3-Sb_2O_5-Pd-doped SnO_2 + Pd-coated layer, La_2O_5-$PdCl_2$-doped SnO_2, WO_3-doped SnO_2 + Pt-coated layer and ThO_2-V_2O_5-$PdCl_2$-doped SnO_2. The small-sized gas identification instrument is composed of a GMS 81504 containing an internal ROM (4k bytes), a RAM (128 bytes), four-channel AD converter as MPU, LEDs for displaying alarm conditions for three gases and interface circuits for them. The system has been used to identify three levels (LPG/LNG alarm, CO alarm and No alarm) and the identification has been successfully demonstrated. This result clearly shows that the small-sized gas identification instrument can be effectively used as a leakage alarm device for LPG/LNG and CO gases.

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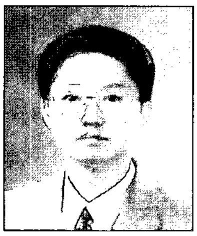

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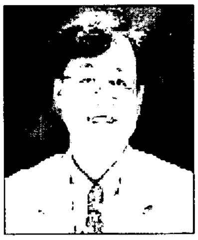

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