Sensor Array based on Metal Oxide Semiconductors for Detecting Gas Mixtures and Its Sensing Properties

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Keywords: Gas Sensor Array, Gas Mixture, Metal Oxide Semiconducting Materials, MEMS Micro Sensor.

Abstract: Metal oxide semiconductor (MOS) gas sensors are very attractive owing to their low cost simplicity of use, large number of detectable gases and various potential application fields. However, the MOS gas sensor has a serious shortcoming of low selectivity in a mixture of gases, In this study MOS micro gas sensors were fabricated for detecting carbon monoxide (CO), nitrogen oxide (NO_2), ammonia (NH_3) and formaldehyde (HCHO) gases, as well as their binary mixed gas systems. Four sensing materials, Pd-SnO_2 for CO, In_2O_3 for NO_X, Ru-WO_3 for NH_3, and SnO_2-ZnO for HCHO were synthesized using a sol-gel method and deposited in the middle of sensor platform. The micro gas sensor platform was fabricated by using a MEMS technology. The sensing electrode and micro heater were designed to be a co-planar type structure with the Pt thin film layer. The gas sensitivity and sensing behaviour for gas mixtures suggested that the selective adsorption of one gas with respect to others occurred for gas mixture and resulted in good selectivity for a particular gas species. Furthermore, the careful pattern recognition of sensing data obtained with sensor array makes it possible to distinguish a gas species from gas mixture and to measure its concentration.

1 INTRODUCTION

Metal oxide semiconductor (MOS) gas sensors are some of the most studied groups of gas sensors owing to their low cost, simplicity of use, and large number of detectable gases and various potential application fields. On the other hand, MOS gas sensors have serious shortcomings of their low selectivity, response drifts and environmental influences such as temperature, vibrations and the gas flow (Korotcenkov, 2005). For practical applications, MOS gas sensors have four major issues of concern: selectivity, long-term stability, reproducibility of the devices, and sensitivity.

Regarding the selectivity issue, the electronic nose (e-nose) concept has been developed to achieve the ability of classifying complex gas mixtures, such as aromas and odors, using cross-sensitive sensors (Weimar, 1998). In general, an e-nose system utilizes gas sensing signals within the sensor array, and the characteristics of individual sensors should be as diverse as possible to ensure that the partial sensor gas responses are not correlated for the reliable discrimination of a certain gas from gas mixture. As other issues related to the long-term stability and reproducibility, such e-nose systems require good reproducibility of the sensor array and high training cost for sensor maintenance. This appears to be one of key challenges requiring the breakthrough (Eranna, 2004).

Gas identification techniques have attracted considerable attention over the past twenty years. The ability to monitor the leakage of combustible and explosive gases is essential for preventing accidental explosions and problems with the pollution and the toxicity. Accordingly, there is urgent demand for sensors combined with pattern recognition systems that can detect and determine the various kinds of combustible gases selectively (Zhang, 2008). In previous studies, we developed four different MEMS-type gas sensors for the detection of carbon monoxide (CO) (Kim, 2007), nitrogen oxides (NO_x) (Yoon, 2009), ammonia (NH_3) (Lee, 2010), and formaldehyde (HCHO) (Kim, 2012). Four sensing materials with nano-sized particles for these target gases (Pd-SnO_2 nano-powder for CO, In_2O_3 nano-particle for NO_X, Ru-WO_3 nano-composite for NH_3, and hybridized SnO_2-ZnO material for HCHO) were synthesized using a sol-gel method. Each MEMS gas sensor showed good sensing performance for its target gas, and the optimal operating temperature was determined.

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In this study, micro-hotplate-based MOS gas sensors, which have a number of interesting features and are particularly attractive for their practical approach, were utilized for the detection of gas mixtures. The sensing responses of four sensors were investigated for the gas mixture, particularly binary mixed gases along CO, NO_x, NH_3, and HCHO. Then, selectivity and response pattern for these sensors to a particular gas along mixed gases were examined.

2 EXPERIMENTAL

2.1 Preparation of Sensing Materials

The appropriate sensing materials for four different gases; SnO_2 for CO (designated as SN sensor), In_2O_3 for NO_X (IN sensor), WO_3 for NH_3 (WO sensor), and SnO_2-ZnO for HCHO (SZ sensor), were synthesized using the sol-gel based method. Figure 1 shows field emission scanning electron microscopy (FESEM) images of the four sensing materials. The average particle sizes were 40 nm for SN, 70 nm for IN, 1,000 nm for WO, and 20 nm for SZ sensors, respectively.

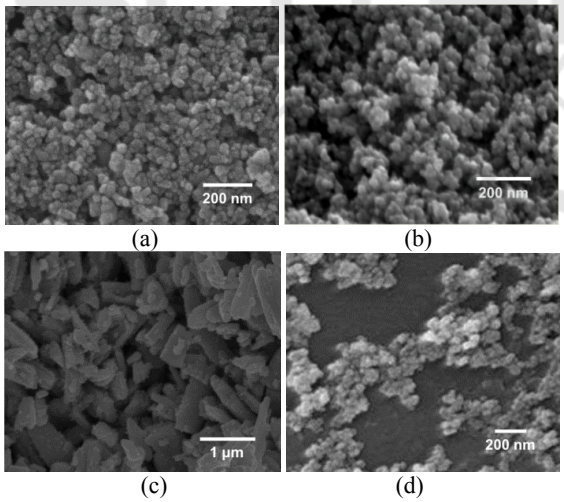


Figure 1: Micro-structures of the four gas sensing materials: (a) Pd-SnO_2, (b) In_2O_3, (c) Ru-WO_3, and (d) Pd doped SnO_2-ZnO.

Each sol-precusor containing its sensing element was dripped with a micro-pipet on the electrode of sensor platform, and then heat-treated at its appropriate sintering temperature. Table 1 represents main features of sensing materials and the optimum temperature for their gas sensing.

Table 1: Main features of four different sensing materials.

	Composition	Average Particle Size	Optimum Temp. (°C)
SN	1% Pd-SnO_2	40 nm	225
IN	In_2O_3	70 nm	225
WO	1% Ru-WO_3	1.0 μm	367
SZ	1% Pd + SnO_2-ZnO	20 nm	367

2.2 Fabrication of MEMS-based Sensors

Micro gas sensor platforms were designed with co-planar type in which sensor electrode and micro-heater were existed on the identical film (Pt thin film) layer, and fabricated using the MEMS process, previously (Choi, 2012). The sensor chip size of the MEMS platform was 1.8 mm × 1.8 mm, and the membrane located in the central part of the sensor chip was 0.9 mm × 0.9 mm. Figure 2(a) shows the photograph of the IN sensor device with TO-39 package in which the sensor chip was placed and connected to the electric terminals by Au wires. The fabricated sensor had low power dissipation, and its power consumption increased linearly with increasing operation temperature as shown in Figure 2 (b). For example, power consumptions operated at 225°C for the SN sensor and 367°C for the WO sensor were 35.26 and 64.37 mW, respectively.

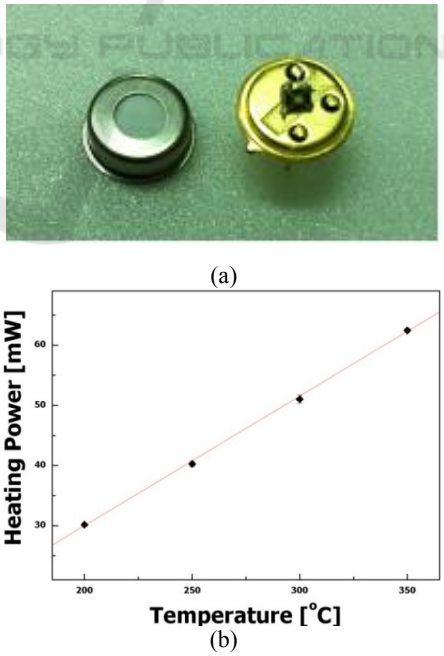


Figure 2: (a) Photograph of fabricated sensor on the TO-39 package and (b) electro-thermal characteristic as the heating power vs. operating temperature.

2.3 Measurement of Sensing Response

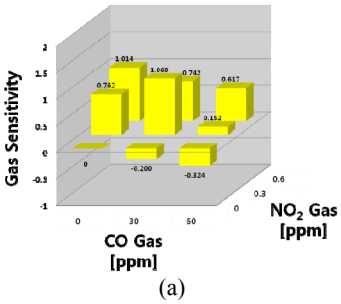
The sensing properties were tested for gas mixture in a gas chamber in which four gas sensors were placed. The gas chamber was connected to a computer-supervised continuous gas flow system that produced the desired concentration for each gas and gas mixtures with a good reproducibility. The test gases (CO, NO_X, NH_3, and HCHO) were diluted with a nitrogen gas and carried by dry air at a constant flow rate. The total gas flow rate was about 500 ml/min. The concentration of each test gas was 0 ~ 60 ppm for CO, 0~0.6 ppm for NO_2, 0 ~ 10.0 ppm for NH_3, and 0 ~ 5.0 ppm for HCHO, respectively.

To quantify the sensor response for both oxidizing and reducing gases as well as their mixtures, the gas sensitivity (S) was defined as $S = \log (R_g/R_a)$, where R_a is the sensor resistance in air and R_g is the sensor resistance after injecting the test gas. The gas sensitivity showed negative values ($S < 0$) for reducing gases, and positive values ($S > 0$) for oxidizing gases because all sensors were simultaneously sensitive to both reducing (CO, NH_3 and HCHO) and oxidizing (NO_2) gases. The gas sensing properties and selective reactions to several gases were analyzed by quantifying the sensitivity.

3 RESULTS AND DISCUSSION

3.1 Sensing Response for CO-NO_2 Gas Mixture

Figure 3 shows the variations of the gas sensitivity of all sensors to CO and NO_2 gases and their mixture. The SN and IN sensors showed stronger responses to NO_2 gas than CO, and their sensitivities showed positive values in the presence of NO_2 gas. The SN sensor exhibited a strong response to both gases and their mixtures, whereas the IN sensor responded only to NO_2. The WO and SZ sensors exhibited similar behaviors to the SN sensor, but their sensitivities to NO_2 gas were slightly lower.



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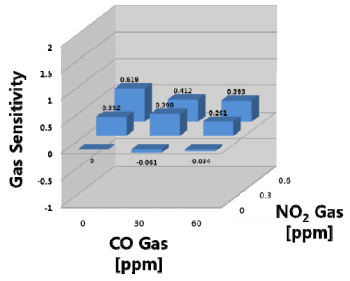

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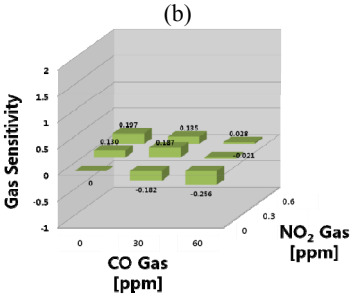

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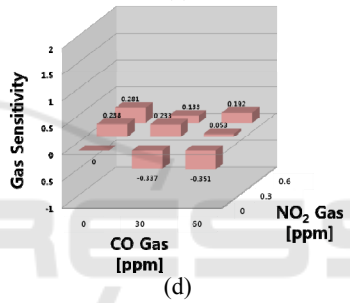


(d)

Figure 3: Gas sensing properties in the CO-NO_2 system; (a) SN, (b) IN, (c) WO, and (d) SZ sensors.

3.2 Sensing Response for CO-NH_3 Gas Mixture

In the CO-NH_3 gas mixture, the CO gas responses were much higher than NH_3 gas in a mixture of reducing agents, but the sensitivities in the gas mixture were higher than that to each gas separately under most experimental conditions (Figure 4). The SN and SZ sensors were more sensitive to their target gas (CO) than NH_3 within the test ranges: S = -0.179 and -0.420 for SN, and S = -0.100 and -0.176 for SZ sensors (at CO 30 ppm and 60 ppm). On the other hand, the changes in resistance were slightly lower in the case of a gas mixture. The IN sensor responses were quite poor to both CO and NH_3 gases. The WO and SZ sensors were sensitive to both the single gases and their mixtures, with higher sensitivities observed with the gas mixtures. For the tests in a mixture of reducing agents, the sensor responses targeting these gases did not show any synergic effects. The sensitivity of the SN sensor was -0.420 for 60 ppm CO gas, but the sensitivity

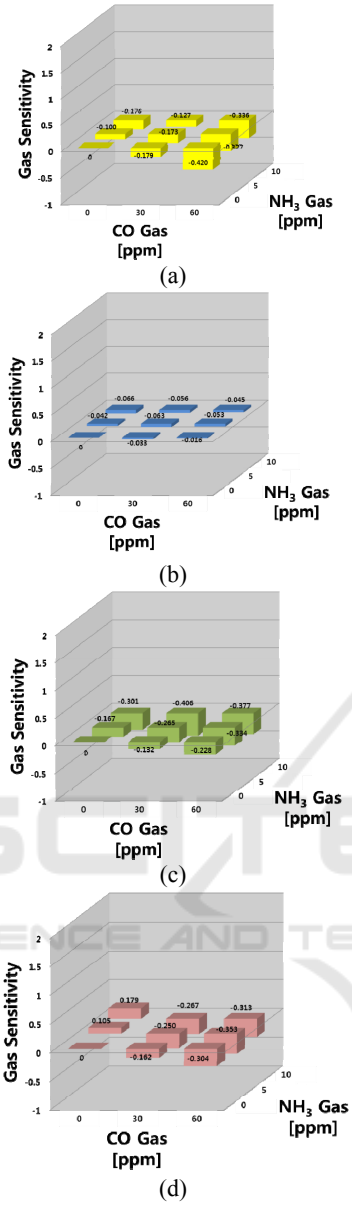


Figure 4: Gas sensing properties in the CO-NH_3 system; (a) SN, (b) IN, (c) WO, and (d) SZ sensors.

was slightly lower (S = -0.327) for CO 60 ppm – NH_3 2.5 ppm. This phenomenon was not observed in the other sensors, which had gas selectivity for the specific gas species. In three mixtures (CO 60 ppm – NH_3 0 ppm, CO 60 ppm – NH_3 5.0 ppm, and CO 60 ppm – NH_3 10.0 ppm), the CO concentration was identical. As the NH_3 concentration increased, however, the sensitivity of the SN sensor was slightly lower for the gas mixtures than for the single CO gas. This suggests that the specific adsorption and selective activation of adsorption sites might occur in gas mixtures and offer a priority for the adsorption of a specific gas, which will be discussed in the following section.

3.3 Sensing Response for NO_2-NH_3 Gas Mixture

In the NO_2-NH_3 gas mixture, as shown in Figure 5, the responses to NO_2 gas were stronger than those of NH_3. In the SN sensor, the sensitivities exhibited increasing behavior to NO_2 and decreasing behavior to NH_3 at higher concentrations, showing that the sensor responds to both gases (S = 0.934 at 0.3 ppm).

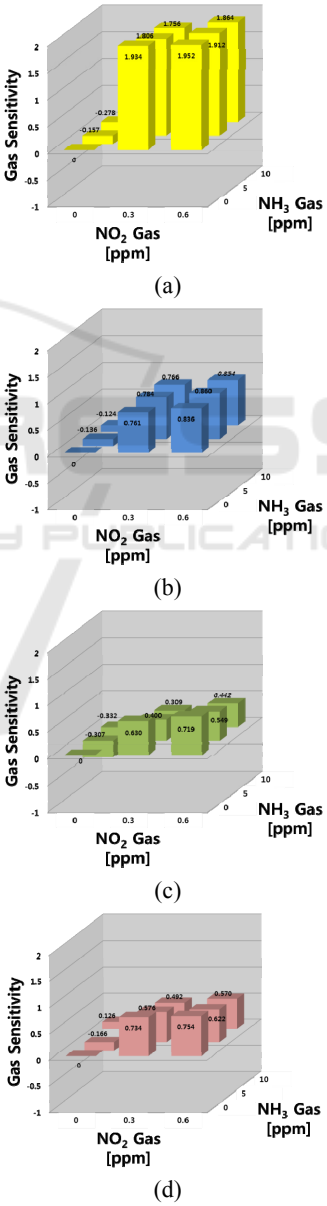
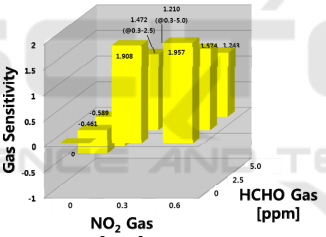


Figure 5: Gas sensing properties in the NO_2-NH_3 system; (a) SN, (b) IN, (c) WO, and (d) SZ sensors.

In the gas mixtures, the changes in resistance were higher than the baseline (Ra) and decreased with increasing NH_3 concentration. On the other hand, the sensitivities to both gases had positive values ($S > 0$) within the test ranges. The IN sensor had a selective response to NO_2 gas but was barely sensitive to NH_3 gas. As the NH_3 gas concentration increased, the IN sensor exhibited a slight decrease in sensitivity to NO_2 gas in the NO_2-NH_3 mixed gas system. The WO sensor showed similar behaviour to the IN sensor, but it was a little more sensitive to NO_2 gas.

3.4 Sensing Response for NO_2-HCHO Gas Mixture

In the NO_2-HCHO system, the responses to NO_2 gas were stronger than those of HCHO (in Figure 6). In the SN and WO sensors, the sensitivities showed increasing behavior to NO_2 and decreasing behavior to HCHO at higher concentrations. On the other hand, the IN sensor is selective to NO_2 gas, since it shows no response to HCHO gas. As the HCHO gas concentration increased, the IN sensor showed a slight decrease in sensitivity to NO_2 gas in the NO_2-HCHO mixed gas system. The WO sensor showed similar behavior to the IN sensor, as it is selective to NO_2 gas. The SZ sensor responses toward HCHO were stronger than NO_2 gas for the NO_2 and HCHO gas mixture.



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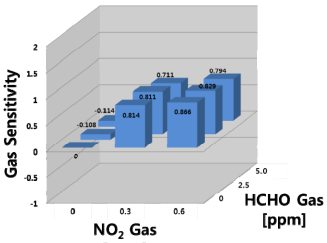

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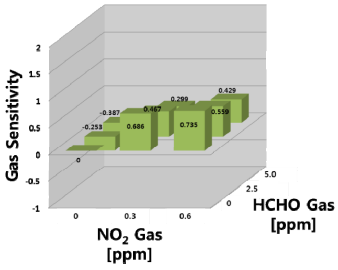

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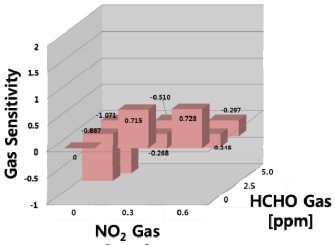

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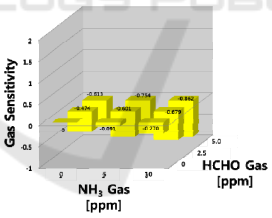
Figure 6: Gas sensing properties in the NO_2-HCHO system; (a) SN, (b) IN, (c) WO, and (d) SZ sensors.

3.5 Sensing Response for NH_3-HCHO Gas Mixture

For the NH_3-HCHO system as shown in Figure 7, the IN sensor did not respond to any of gases; NH_3 and HCHO, three other sensors (SN, WO and SZ) were sensitive to either single gas or its mixture. The SZ sensor is selective to HCHO. In this mixture of two reducing gases, there was no synergic effect in the SN sensor responding to both NH_3 and HCHO gases.



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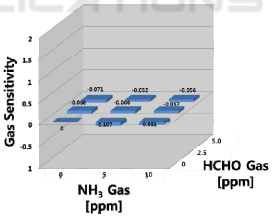

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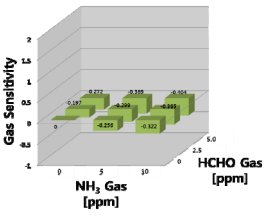

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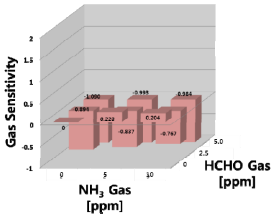

(d)

Figure 7: Gas sensing properties in the NH_3-HCHO system; (a) SN, (b) IN, (c) WO, and (d) SZ sensors.

3.6 Discussion

The present study analyzed the sensing properties of micro gas sensor arrays by examining the raw data

in the gas mixtures. Overall, the IN sensor could detect NO_2 selectively, whereas the SN sensors detected all four gases (CO, NO_2, NH_3 and HCHO). If coupled with an IN sensor, SN is capable of detecting NO_2 sensitively. On the other hand, the gas sensitivity signals of the two sensors were not sufficient for the detection of all four gases. The WO and SZ sensors detected all four gases but had low gas selectivity. Therefore, the four-sensor-array would be sufficient to discriminate mixtures of these gases. To gain clear insight into the applicability of the sensor array in this application, the responses with sensitivity can be arranged in a 4×4 matrix, in which each element represents the response of each sensor to each target gas. This matrix suggests how the different gas contributions can be extrapolated from the sensor array data using the signal process.

4 CONCLUSIONS

The sensing properties for the MEMS-based MOS gas sensors were investigated with gas mixtures along CO, NO_X, NH_3, and HCHO gases. Four different gas sensors were fabricated for the detection of CO, NO_X, NH_3, and HCHO gases, respectively. Each sensor exhibited good sensitivity to its target gas, and the optimum operating temperature of micro-heater was examined. The sensing response behaviors for gas mixture were analyzed using the experimental data in the MEMS gas sensor arrays with respect to selectivity and response pattern. The gas sensing behaviors in mixed gas systems suggest that specific adsorption and selective activation of adsorption sites might occur in gas mixtures and offer priority for the adsorption of a specific gas. An analysis of the sensing performance of the sensor arrays will make it possible to discriminate the components in harmful gas mixtures as well as their concentrations using pattern recognition techniques.

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