Sensors and Materials, Vol. 17, No. 2 (2005) 077–085
MYU Tokyo

S & M 0588

Portable Electronic Nose System Utilizing Single Gas Sensor Array Fabricated by Si Bulk Micromachining

Yoonseok Yang**, Seung-Chul Ha and Yong Shin Kim*

Bio-MEMS Team, Electronics and Telecommunications Research Institute,
161 Kajong-dong, Yusong-gu, Daejeon 305-350, Korea

(Received April 10, 2004; accepted November 16, 2004)

Key words: gas sensor array, electronic nose, carbon-black-polymer composite, Si bulk micromachining, pattern recognition

A portable electronic nose system has been developed utilizing a single 16-channel sensor array chip. It was fabricated by Si bulk micromachining and equipped with the sensing materials of carbon-black-polymer composites. This system consists of a small sensing module containing the sensor array chip, signal processing circuits and vapor delivery components on a printed circuit board, and a laptop personal computer equipped with data acquisition and pattern recognition programs. Experimental results show that the sensor array chip can measure and recognize volatile organic compounds even by simple principle component analysis. In addition, our portable electronic nose system has successfully classified real complex samples, i.e., brandy and whiskey.

1. Introduction

The development of micro-electromechanical systems (MEMS)-based gas sensor arrays is a rapidly growing area of research due to their low power consumption, the possibility of mass production by batch fabrication, and selectivity improvements through the use of arrays. The microfabricated sensor array is attractive for use in a portable electronic nose (E-Nose) system which has applications in many fields, such as environmental monitoring, pollution measurement, food quality control, and medical diagnosis.[1–5]

Recently, arrays of broadly responsive sensors fabricated from the composites of carbon black and insulating organic polymers have received significant attention for their potential use in the classification, identification, and quantification of analyte vapors.[6–10]

*Corresponding author, e-mail address: yongshin@etri.re.kr
**Present address: Division of Bionics and Bioinformatics Engineering, Chunbuk National University, Jeonju 561-156, Republic of Korea

Various carbon-black-polymer composite detectors can be fabricated by choosing the species and regulating the quantity of the insulating organic chemicals. These sensors enable the fabrication of very small size, low-power, and light-weight detector arrays. For example, Zee *et al.* reported the microfabrication of carbon-black composite detectors with sizes from 0.5×0.6 to 0.1×0.1 mm^2 using MEMS technology.[11] These detectors were able to detect simple organic volatile chemicals, and there was no significant reduction in response magnitude due to the reduction of a sensing area.

In this work, we present the notebook-based portable E-Nose system utilizing a miniaturized sensor array, electrical and mechanical hardware, and data acquisition and recognition software. The sensor array was embodied by the microfabrication of a silicon wafer and by drop coating carbon-black composite solutions. This is our first step toward realizing a small E-Nose device capable of being operated with a personal digital assistant (PDA) for the noninvasive health monitoring application. In future work, we will continuously try to miniaturize the E-Nose device by the integration of on-chip circuits and MEMS components, such as a valve and preconcentrator.

2. Embodiment of E-Nose System

2.1 *Basic structure and operation of our portable E-Nose*

A schematic of the portable E-Nose, showing all the vital processes performed by our instruments, is shown in Fig. 1. The portable E-Nose consists of two major modules, i.e., the sensing module and the laptop personal computer (PC). The sensing module is sufficiently small to be held by hand. It consists of vapor delivery components, namely an inlet port and a mini diaphragm pump, and a sensing chamber with a sensor array chip on a printed circuit board (PCB) with signal conditioning and amplification circuits. Measured multichannel analog signals are delivered to the A/D card (NI, DAQ 6062E)

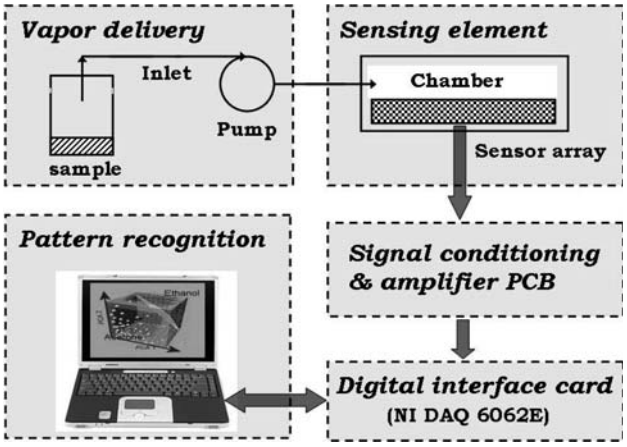


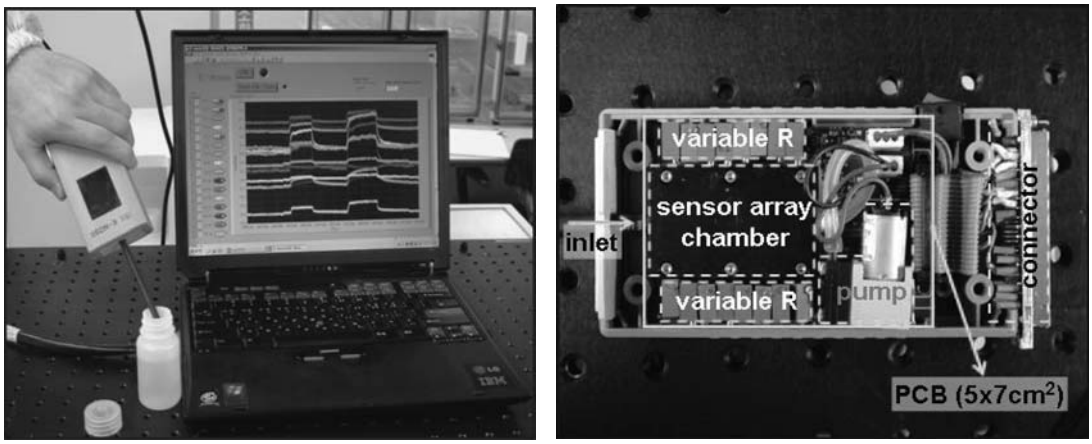
Fig. 1. Block diagram of our electronic nose system.

connected to the laptop PC. The data acquisition and pattern recognition are performed by the user software programmed in LabView (NI) and MatLab (MathWorks) environments. This first prototype uses the 'pumping only' sampling scheme, in which test gas is pumped into the measurement chamber and pumped out through an exhaust, even though this scheme is insufficient for a commercial product. To upgrade the sampling method of our prototype instrument, we are going to adopt more sophisticated components, such as a valve, filter, and preconcentrator.

Figure 2 shows our prototype E-Nose system. The analysis procedure is as follows: 1) transfer analyte into a sample bottle, 2) turn on the sensing module and wait for the initial resistances of the sensors to stabilize while pumping is carried out in ambient, 3) move the inlet port to the sample bottle and maintain their positions for the measuring duration of 10–60 s, 4) take out the inlet port and wait for the sensor response to recover to its initial position, 5) process the measured data for pattern recognition. With this system, it is possible to acquire and display the measured signals of up to 16 channels in realtime, as shown in Fig. 2(a). The arrangement of components inside the sensing module is shown in Fig. 2(b). The variable resistors are used to regulate the signal baselines, and their magnitudes are set to the initial resistances of each sensor to obtain maximum sensitivity. The PCB size which determines the size of the sensing module is 5×7 cm^2.

2.2 *Fabrication of single 16-channel sensor array chip using Si bulk micromachining*

A key element of our E-Nose system is the miniaturized gas sensor array, as shown in Fig. 3. The sensor array has independent sensing elements for 16 channels integrated on a single silicon substrate. The detailed fabrication process using four photomasks has been reported previously.[12,13] Ten sensor array chips are fabricated on a 5-inch Si wafer using the batch process. Figure 3(a) shows an image of a sensor array chip obtained by sawing



(a) (b)

Fig. 2. Photographs of (a) our E-Nose system and (b) internal arrangement of components.

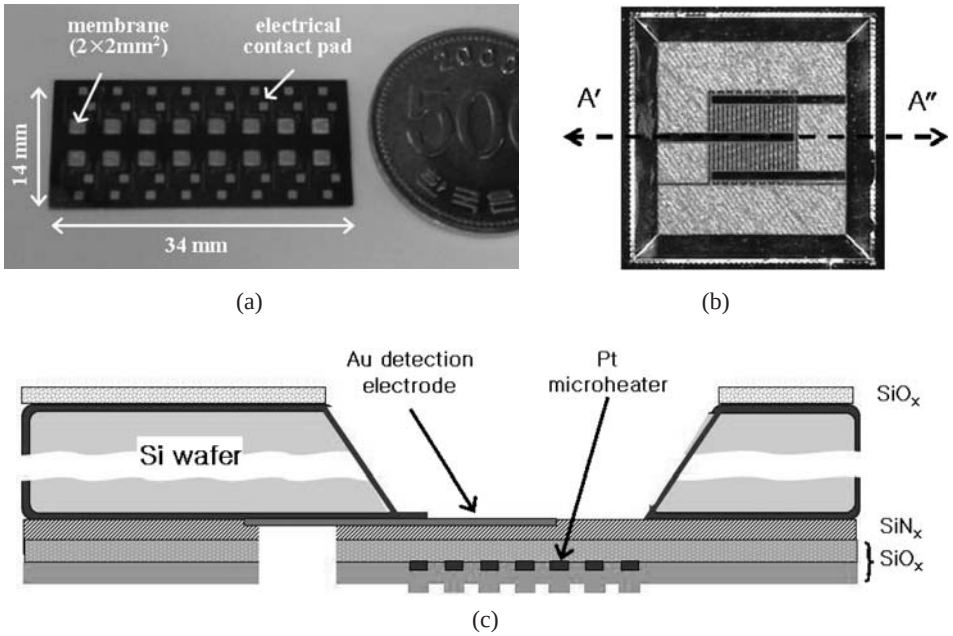


Fig. 3. (a) Single 16-channel gas sensor array fabricated by Si-bulk micromachining and microfabrication; (b) optical image of one sensor element; (c) cross-sectional schematic structure along the direction from A′ to A″ in (b).

the wafer. The array chip has the size of 14×34 mm^2. Each sensing element has a square membrane with an area of 2×2 mm^2 to minimize heat loss into the Si substrate and to avoid temperature crosstalk with neighboring cells (see Fig. 3(b)). The bulk-micromachined membranes allow the carbon-black-polymer composite solution to be placed reproducibly in specific and well-constrained areas during the drop-coating process. Inside each membrane, there are interdigitated detection electrodes of 100-μm width and 300-μm spacing for sensing the resistance variation of a chemiresistive sensor, and an embedded Pt microheater (25-μm width and spacing) surrounded by insulating oxide and nitride layers for regulating the temperature of the sensing materials constantly. Figure 3(c) displays the cross-sectional schematic structure along the horizontal center line shown in Fig. 3(b). The membrane structures are fabricated by the micromachining process using the anisotropic wet etching of bulk Si as the final fabrication step. The wet etching is carried out using a 5 wt% tetra-methyl ammonium hydroxide (TMAH) solution. TMAH solution is maintained at the temperature of 85°C and is stirred to promote active and homogenous etching reactions. To maintain the concentration of TMAH during the etching process, the vaporized chemicals were condensed and returned to the reaction bath. The end point of the etching process is confirmed by checking the resistance of the electrical connection pads with the relatively large area of 1×1 mm^2. The fabrication flow is considered to be compatible with the conventional CMOS process, which means it is possible to equip the sensor array chip with signal processing circuitry.

2.3 *Selection and fabrication of carbon-black-polymer composite sensors*

The individual sensor elements are constructed from films consisting of carbon-black particles dispersed in insulating organic polymers. The carbon black endows the films with electrical conductivity, whereas different organic polymers are the source of detection diversity among the elements in the sensor array. The swelling of the polymer upon exposure to a vapor increases the resistance of the film, thereby providing an extraordinarily simple means for monitoring the presence of a vapor.[6,14] In addition, additive plasticizers, such as bis(2-ethylhexyl) phthalate and di(ethylene glycol) dibenzoate have been reported to induce a fast response and further diversity in the vapor detection characteristics of the composite sensors.[15] The detection performance and characteristics of sensor elements, which had various combinations of insulating polymer, plasticizer, and carbon black, were tested upon exposure to several simple organic vapors. From this study, we selected the sensor elements that had a high sensitivity to the simple vapors and long-term stability during operation. The selected carbon-black-polymer composites used in our E-Nose system are summarized in Table 1.

Composite solutions were made by mixing carbon black with the content of 15–20 wt.% and the polymers listed in Table 1. The carbon black used was either Pearls 2000 or 700 from Cabot, depending on the required resistance of the composite film. After sonicated for approximately 10 min to achieve a good dispersion of the carbon-black particles, the composite solution with a volume of 1.5–3.5 μl was deposited using an automated micropipette into the membrane well which houses the interdigitated detection electrodes. After dispensing the solution, solvent was immediately evaporated within 60 s leaving a composite film. The drop-coating process was repeated until the resistance of the sensors was in the range of 10 kΩ–10 MΩ. The micromachined well helped to contain the solution in the designated position and prevented the solution from spreading to other

Table 1
Carbon-black-polymer composition used in our electronic nose system.

Sensor	Polymer
S1	poly(stylene-co-allyl alcohol)
S2	poly(4-methylstyrene)[a]
S3	poly(caprolactone)
S4	Polystyrene-black-polyisoprene-black-polystyrene
S5	cellulose acetate
S6	poly(stylene-co-methyl methacrylate)
S7	poly(styrene-co-butadiene)
S8	poly(vinyl stearate)
S9	hydroxypropyl cellulose[b]
S10	poly(butadiene)
S11	poly(vinyl butyral)-co-vinyl alcohol-co-vinyl acetate
S12	ethyl cellulose
S13	poly(vinyl acetate)[b]

[a] Plasticized with 50% bis(2-ethylhexyl) phthalate by mass.
[b] Plasticized with 50% di(ethylene glycol) dibenzoate by mass.

regions. It is possible to control the thickness of the deposited composite film by adjusting the dispensing volume, and also to achieve reproducible film formation.[13]

2.4 *Sensor interface circuitry*

Sensor interface circuitry constitutes the first stage of electrical instrumentation. The purpose of this circuitry is to generate an electrical signal that reflects physical or/and chemical changes induced in the sensor by vapor exposure. In chemiresistive sensors, exposure to volatile compounds changes the conductance of the sensing film. Figure 4 shows the interface circuitry used in this study. It consists of a voltage divider and amplification circuits. The voltage divider is a standard circuit used for measuring large resistance changes and the amplification circuit is used to maximize the detection sensitivity by amplifying the output voltage so that it is appropriate for the input level of the A/D card. A typical value of amplification gain was 10.

3. Evaluation of E-Nose System

3.1 *Vapor sensing performance to simple volatile organic compounds*

To evaluate the fabricated sensor array chip, the responses of sensor elements were measured for simple volatile organic compounds (VOCs), i.e., single organic solvents such as methanol, ethanol, benzene, and acetone. Figure 5 shows the typical response profile of the ethyl cellulose composite sensor (S12 in Table 1) as a function of time exposed to ethanol. The concentration of ethanol was regulated to be 1000–5000 ppm in synthetic dry air. It exhibits a linear increase of the response magnitude with increasing ethanol analyte concentration. In addition, the response time is found to be very fast: the rise time of ~20 s and the decay time of ~45 s, where the rise and decay times are defined as the time taken to reach 90% of the peak maximum and the time to recover to 10%, respectively.

The classification of VOCs in the E-Nose system is performed by running a pattern recognition algorithm with characteristics, namely feature parameters, obtained from the

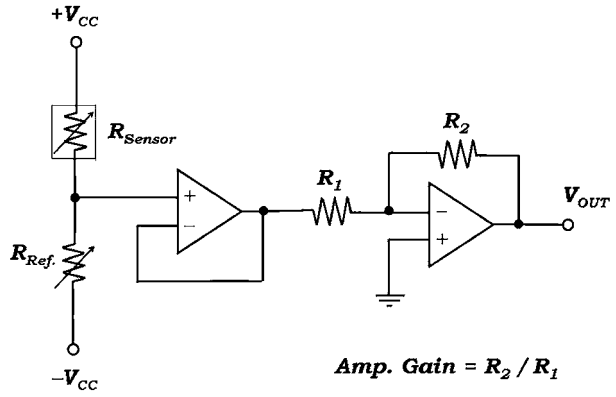


Fig. 4. Schematic diagram of sensor interface circuitry.

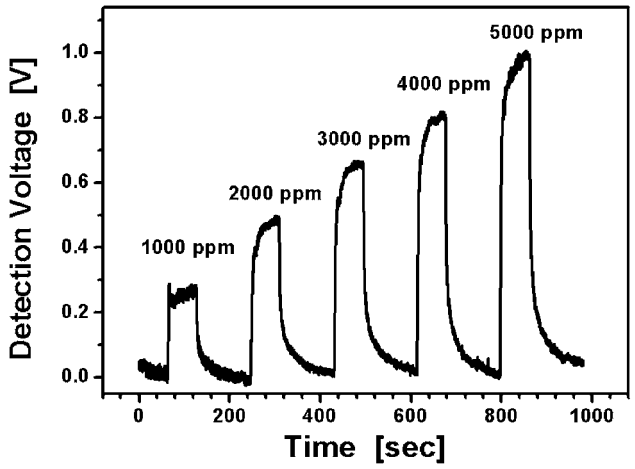


Fig. 5. Plot of detection response as a function of elapsed time with increasing ethanol concentration for ethyl cellulose composite sensor, S12.

responses of arrayed sensor elements. The representative characteristic used in our chemiresistive sensors is the percentage ratio of the maximum resistance change with respect to the initial resistance

$$S = 100 \times (R - R_0) / R_0 , \tag{1}$$

where S is defined as the detection response, R as the maximum resistance of the sensor, and R_o as the stabilized initial resistance. These parameters are simultaneously measured for the individual elements of our sensor array. Figure 6 shows bar plots of the normalized response patterns obtained for the four simple VOCs with a concentration of 5000 ppm. It shows different pattern shapes among analytes, which makes it possible to classify the chemicals utilizing a pattern recognition program. Actually, successful classification could be promoted by the principal component analysis (PCA): there were clearly observed boundaries among results measured from different analytes in coordinates of PCA.

3.2 *Case study using our E-Nose system: classification of brandy and whiskey*

The prototype E-Nose system was applied to real samples having complex constituents to evaluate its potential performance at a job site. As the first case study, we chose the classification of liquors, namely brandy (Hennessy VSOP) and whiskey (Johnny Walker Red Label). After being placed into small sample bottles, these samples were analyzed according to the standard operation method described above. Figure 7 shows PCA analysis results obtained from repetitive measurements, 42 times for the brandy and 25 times for the whiskey. The results clearly demonstrate that our portable E-Nose system can successfully classify the liquors. For identification of unknown sample, we used the pattern recognition

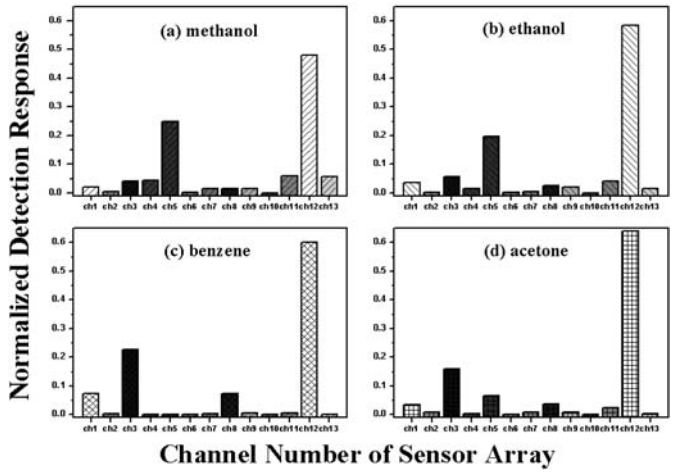


Fig. 6. Bar plots of normalized detection responses obtained from the single sensor array chip for four different organic vapors: (a) methanol, (b) ethanol, (c) benzene, and (d)acetone.

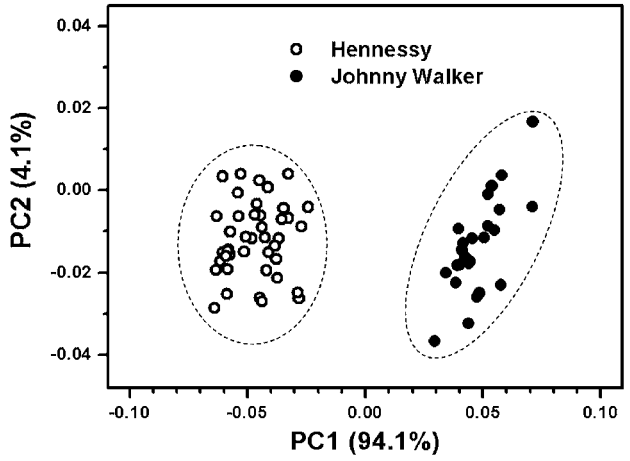


Fig. 7. PCA analysis results showing the classification of brandy (Hennessy VSOP) and whiskey (Johnny Walker Red Label). The PC1 and PC2 of x- and y-axes correspond to the two main components with the largest contribution in PCA space. The percentage on the axes is the magnitude of the contribution.

algorithm of a supporting vector machine (SVM) due to its good performance. The SVM method utilizes optimized boundary surfaces to classify the liquors. Before identifying an unknown liquor sample, we prepare different classification boundary definitions obtained from the training sets displayed in Fig. 7. We could immediately identify whether the unknown sample was the brandy or the whiskey by using the SVM classification definition and the feature parameters obtained from the unknown sample at the job site.

4. Conclusion

As our first step toward realizing a small E-Nose device capable of being equipped within a PDA, we presented here a portable E-Nose system utilizing a laptop PC, and demonstrated the successful classification of real complex samples, i.e., brandy and whiskey. The key elements of our E-Nose system are the single sensor array chip fabricated by Si bulk micromachining and the carbon-black-polymer composite sensors. In future work, we will continuously try to miniaturize and improve our E-Nose device through the integration of on-chip circuits and MEMS components, such as a valve and preconcentrator.

Acknowledgement

This work was supported by the Ministry of Information and Communication of Korea and the Ministry of Science and Technology of Korea through the NRL program.

References

1 T. C. Pearce, S. S. Schffman, H. T. Nagle and J. W. Gardner: Handbook of Machine Olfaction (Wiley-VCH, Weinheim, 2003).
2 J. W. Gardner and P. N. Bartlett: Electronic Noses Principles and Applications (Oxford University Press, New York, 1999).
3 K. J. Albert, N. S. Lewis, C. L. Schauer, G. A. Sotzing, S. E. Stitzel, T. P. Valid and D. R. Walt: Chem Rev. **100** (2000) 2595.
4 C. Hagleitner, A. Hierlemann, D. Lange, A. Kummer, N. Kerness, O. Brand and H. Baltes: Nature **414** (2001) 293.
5 M. Graf, D. Barrettino, P. Käser, J. Cerdà, A. Hierlemann and H. Baltes: Proceeding of the 12th International Conference on Solid State Sensors and Actuators (Transducers '03) (Boston, 2003) p. 123.
6 M. C. Lonergan, E. J. Severin, B. J. Doleman, S. A. Beaber, R. H. Grubbs and N. S. Lewis: Chem. Mater. **8** (1996) 2298.
7 A. R. Hopkins and N. S. Lewis: Anal. Chem. **73** (2001) 884.
8 S. M. Briglin and N. S. Lewis: J. Phys. Chem. B **107** (2003) 11031.
9 B. J. Doleman, R. D. Sanner, E. J. Severin, R. H. Grubbs and N. S. Lewis: Anal. Chem. **70** (1998) 2560.
10 B. J. Doleman, M. C. Lonergan, E. J. Severin, T. P. Vaid and N. S. Lewis: Anal. Chem. **70** (1998) 4177.
11 F. Zee and J. W. Judy: Sensors and Actuators B **72** (2001) 120.
12 S. Ha, Y. S. Kim, Y. Yang, Y. J. Kim, H. Yang and Y. T. Kim: The 5th Korean MEMS Conference (Jeju, 2003) p. 175.
13 S. Ha, Y. S. Kim, Y. Yang, Y. J. Kim, S. Cho, H. Yang and Y. T. Kim: Sensors and Actuators B (in press).
14 E. J. Severin and N. S. Lewis: Anal. Chem. **72** (2001) 884.
15 M. E. Koscho, R. H. Grubbs and N. S. Lewis: Anal. Chem. **74** (2002) 1307.