Fabrication and characterization of silicon-based microsensors for detecting offensive CH_3SH and $(CH_3)_3N$ gases

Kyuchung Lee and Chang-Wu Hur, *Member, KIMICS*

Abstract—Highly sensitive and mechanically stable gas sensors have been fabricated using the microfabrication and micromachining techniques. The sensing materials used to detect the offensive CH_3SH and $(CH_3)_3N$ gases are 1 wt% Pd-doped SnO_2 and 6 wt% Al_2O_3-doped ZnO, respectively. The optimum operating temperatures of the devices are 250°C and 350°C for CH_3SH and $(CH_3)_3N$, respectively and the corresponding heater power is, respectively, about 55mW and 85mW. Excellent thermal insulation is achieved by the use of a double-layer membrane: i.e. 0.2μm-thick silicon nitride and 1.4μm-thick phosphosilicate glass. The sensors are mechanically stable enough to endure the heat cycles between room temperature and 350°C, at least for 30 days.

Index Terms—Silicon-based microsensor, Offensive CH_3SH and $(CH_3)_3N$ gases, Mechanical stability, Sensitivity, Selectivity, Response time, Recovery time

I. INTRODUCTION

The environmental management has become an issue of vital importance in the modern life. The air pollution by the offensive odors from the domestic and industrial sources is one of the most serious environmental problems. To keep the environmental atmosphere under the tight control, it is essential to have a means to measure the odor intensity accurately and handily. Up until now, most measurements have been carried out using rather delicate and complicated systems, thereby necessitating the practice by specialists. The oxide-semiconductor-based gas sensor is a promising candidate for the air pollution detectors and has been introduced into market. The main requirements for gas sensors are high sensitivity and selectivity, short response time, long-term stability and low power consumption. Recently, considerable interest has arisen in the silicon-based micro-gas-sensors fabricated by the thin film and micromachining techniques[1-5] because they meet the above-mentioned requirements and have such additional advantages as accurate temperature controllability, small size, low cost due to the batch production, easy realization of sensor arrays and possibility of on-chip integration with microelectronics. A number of different device structures and sensing materials have been proposed[4-12]. In this paper, the fabrication and characterization of the silicon-based microsensor with the sensing layer of either Pd-doped SnO_2 or Al_2O_3-doped ZnO is reported, which has high sensitivity and reasonably good selectivity to either CH_3SH or $(CH_3)_3N$, respectively. CH_3SH and $(CH_3)_3N$ are the gases most responsible for the offensive odors from the spoiled vegetables and fish/meat, respectively. The excellent thermal insulation of membrane is achieved by the use of a double-layer structure of phosphosilicate glass (PSG) and silicon nitride, which makes possible significantly lowering the power consumption.

II. EXPERIMENTAL

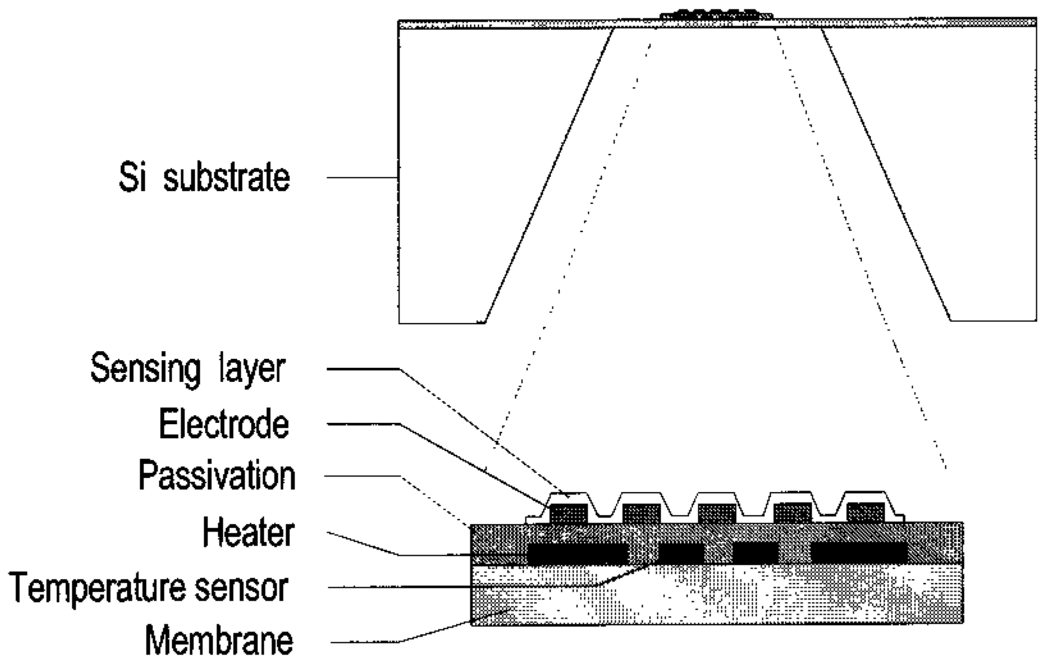

Fig. 1. Cross section of micro-gas-sensor.

As seen in Fig. 1, the device basically consists of stacked layers: gas sensing layer, electrode, insulating layer and Pt heater + temperature sensor formed on the membrane. Five masks were used for the fabrication of sensor. The thin membrane was constructed by the anisotropic etching of silicon substrate and provides excellent thermal insulation, which results in low power consumption. The gas sensitive layers were grown by the r.f. sputter-deposition. The processing steps are:

- Formation of the membrane layer on a silicon substrate,
- Formation of heaters and temperature sensors,
- Deposition of an insulating layer,
- Opening contact holes,
- Formation of electrodes and pads,
- Formation of a sensing layer,
- Backside etching and
- Packaging: slicing/mounting/bonding.

Manuscript received February 25, 2008

Kyuchung Lee, Department of Information Technology, Sungkyul University, 147-2, Anyang-8-dong, Manan-gu, Anyang-city, Gyeonggi-do 430-742, Korea (Email: kclee@sungkyul.edu)

Chang-Wu Hur, Department Electronic Engineering, Mokwon University, Mokwon Gil 21, Seo-gu, Daejeon 302-318, Korea

The detailed fabrication processes are as follows. The base material is a p-type (100) oriented and both-side polished 4" silicon wafer with the thickness of 400 μm. The membrane has to withstand the operating temperature of several hundred degrees in Celsius and should have, among other things, low thermal conductivity, good adhesion property and, in particular, good mechanical stability. Efforts have been made to fabricate membranes using such films as oxynitride[1], silicon-rich nitride[2], oxide-nitride-oxide[3] and silicon dioxide[4-6]. Three different candidates for the electrically and thermally insulating membrane layer were examined: (1) a double-layer of PSG and silicon nitride, (2) silicon nitride and (3) silicon nitride formed on the p^+ layer. The 0.2μm-thick silicon nitride was deposited on both sides of the substrate by low pressure chemical vapor deposition using the SiH_2Cl_2 and NH_3 gases at 800°C. And the 1.4μm-thick PSG was grown only on the front side by atmospheric pressure chemical vapor deposition using the SiH_4, PH_3 and O_2 gases at 450°C. The p^+ layer was formed by the doping with the solid boron source at 1125°C in a diffusion furnace. The boron-doping for 40 min produced the 1.5μm-thick p^+-layer. The thickness of doped layer was indirectly determined by measuring, with secondary electron microscopy, the thickness of the remaining membrane after the backside etching.

The heaters were made of the platinum deposited on a tantalum layer which works as a buffer layer not only to improve the adhesion of platinum onto the underlayer but also to reduce interdiffusion at the processing and working temperatures. Tantalum and platinum were deposited to the thickness of 500Å and 4500Å, respectively, by d.c. sputtering under standard conditions. The Pt/Ta layer was then annealed at 550°C for 30 min. A lift-off process was used to make the heater layer which was passivated by the r.f. sputtered 1μm-thick silicon nitride in the following step. The wafer was subsequently subjected to a photolithography process to define contact holes which were etched out by the reactive ion etching (RIE) process. The electrodes and bonding pads made of the Pt/Ta double-layer were formed on the insulating layer of Si_3N_4. The electrodes were interdigitally patterned and fabricated using a lift-off process as well. The windows for the backside etching were then made by RIE.

The growth parameters for the gas sensing layer were determined using the Taguchi method[13] which is a useful approach when many process parameters are involved. As the gas-sensitive materials, Pd-doped SnO_2 and Al_2O_3-doped ZnO were selected for detecting the CH_3SH and $(CH_3)_3N$ gases, respectively. The films of SnO_2 and ZnO were deposited by r.f. magnetron sputtering and then annealed. A lift-off process was used to pattern the sensing layer. After the deposition of sensing layer, the wafer was backside-etched anisotropically in KOH, thereby leaving behind the thin layers of sensing element and membrane. The sensing layer was protected during the etching process. The chips were mounted on the standard TO-8 packages.

The mechanical stability of the membrane, especially its behavior at high temperature, was examined by subjecting the sensor to the temperature cycles between room temperature and 350°C for 30 days. The measurements of gas sensing properties were carried out in a system fully controlled by a personal computer (see Fig. 2). Response time was measured by exposing the sensors to either 0.2 part per million (ppm) of CH_3SH or 5 ppm of $(CH_3)_3N$. Selectivity was determined by measuring the resistance change of the sensor upon exposure to each gas of CO, C_2H_5OH, CH_3SH and $(CH_3)_3N$.

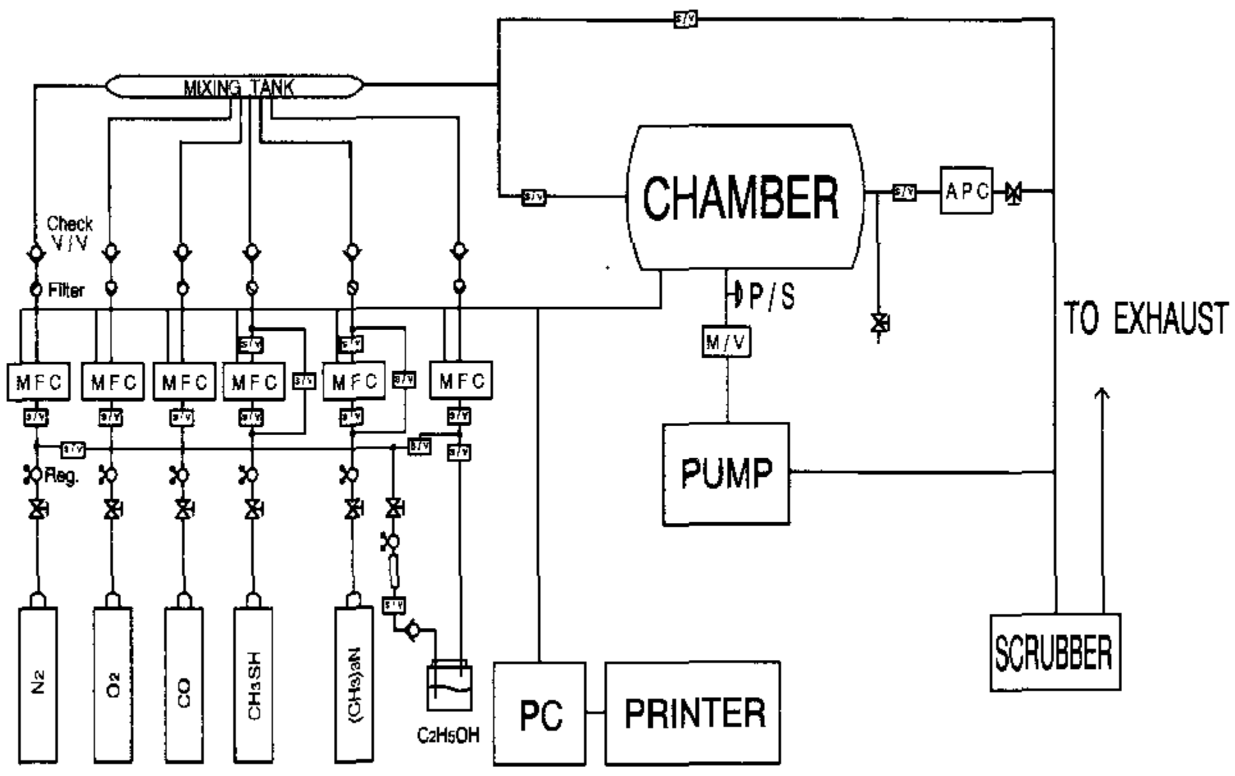

Fig. 2. Schematic diagram of the experimental setup used in this study.

III. RESULT AND DISCUSSION

Table I lists the characteristics of three different membranes: PSG/Si_3N_4, Si_3N_4 and Si_3N_4/p^+.

Table I Characteristics of membranes and heaters

Membrane Thickness	PSG/Si_3N_4 1.4μm/0.2μm	Si_3N_4 0.2μm	Si_3N_4/p^+ 0.2μm/1.5μm
No. of cycles	43,200	8,140	43,200
Heater temp.		Heater power (mW)	
250°C	55	53	220
300°C	70	65	270
350°C	85	78	310

All the membranes except the Si_3N_4 single layer retained the mechanical stability even after subjected to the temperature cycles between room temperature and 350°C up to a period of 30 days (43,200 cycles: 1 cycle = heater on for 30 sec/off for 30 sec). In terms of power consumption, both the Si_3N_4 single layer and the double-layer of PSG and Si_3N_4 turn out to be excellent while the membrane of Si_3N_4/p^+ is rather poor. Taking into account both mechanical stability and power consumption, it is natural to select the double-layer of PSG and Si_3N_4 as the membrane layer.

The heater and temperature sensor made of the Pt:4500Å/Ta:500Å double-layer show good adhesion onto the PSG film. The resistance of the temperature sensor was measured as a function of temperature to calibrate the temperature scale. Next, linearly increasing voltage was applied to the heater and the corresponding current was measured. From the results of these measurements, the temperature versus power relationship was obtained and typical results are presented in Fig. 3. To keep the heater at 250°C or 350°C, about 55mW or 85mW were needed. The power consumption is low enough for most applications[1].

As mentioned earlier, the Taguchi method was used to determine the optimum growth conditions for the sensing layers. Table II lists the Taguchi factors and the growth conditions that yield the best sensitivity for the Pd-SnO_2 and Al_2O_3- ZnO sensors.

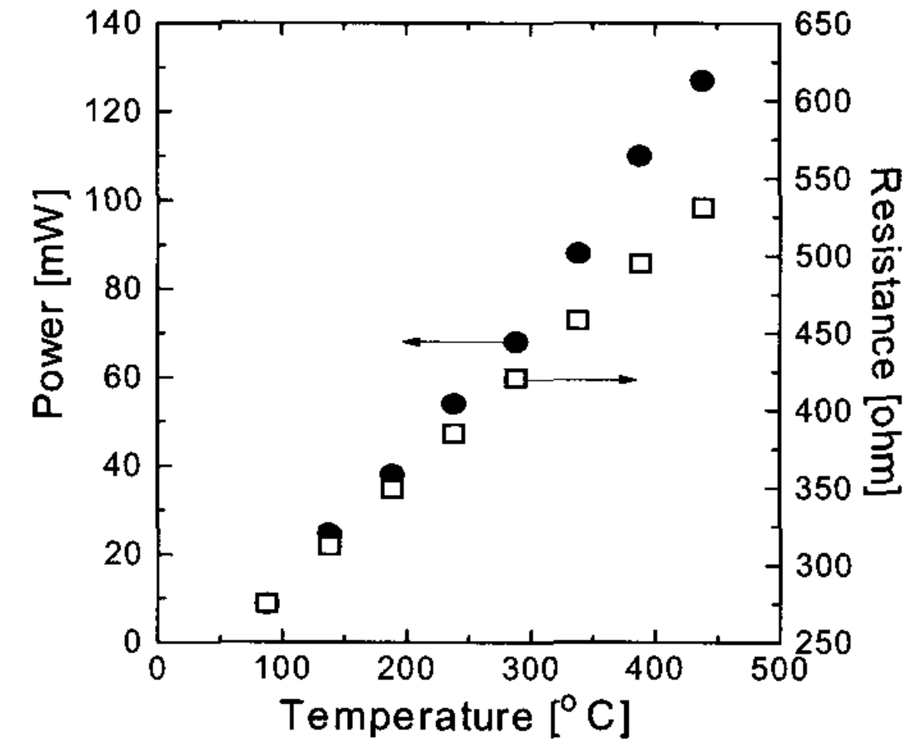

Fig. 3. Heater power and resistance of temperature sensor as a function of temperature.

Table II Taguchi results

Factors	Pd-SnO_2	Al_2O_3- ZnO
Concentration of catalyst	1 wt% Pd	6 wt% Al_2O_3
Working pressure of sputter	50mtorr	30mtorr
O_2 content in sputtering gas	30%	20%
Thickness of sensing layer	2000Å	1000Å
Annealing temperature	450°C	550°C

One of the most important features of any gas sensor is sensitivity, defined as R_a/R_g, where R_a and R_g are the resistances of the sensor, respectively, in air and upon exposure to the gas to be measured. Fig. 4 shows the sensitivity versus CH_3SH concentration at several operating temperatures. While the best results in sensitivity and response time were achieved at the operating temperatures of 300°C and 350°C, respectively, selectivity was poor at the two temperatures. It is apparent from the measurements of sensitivity, selectivity and response time that the optimum operating temperature for the Pd-SnO_2 sensor is about 250°C. As illustrated in Fig. 5, the Pd-SnO_2 sensor has good selectivity to CH_3SH at 250°C.

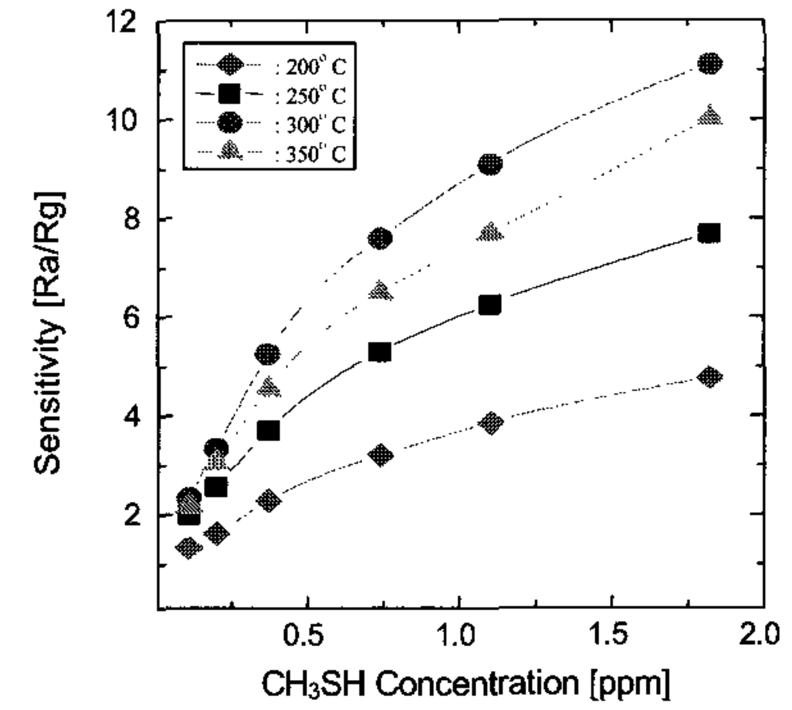

Fig. 4. Sensitivity vs. CH_3SH concentration at various operating temperatures.

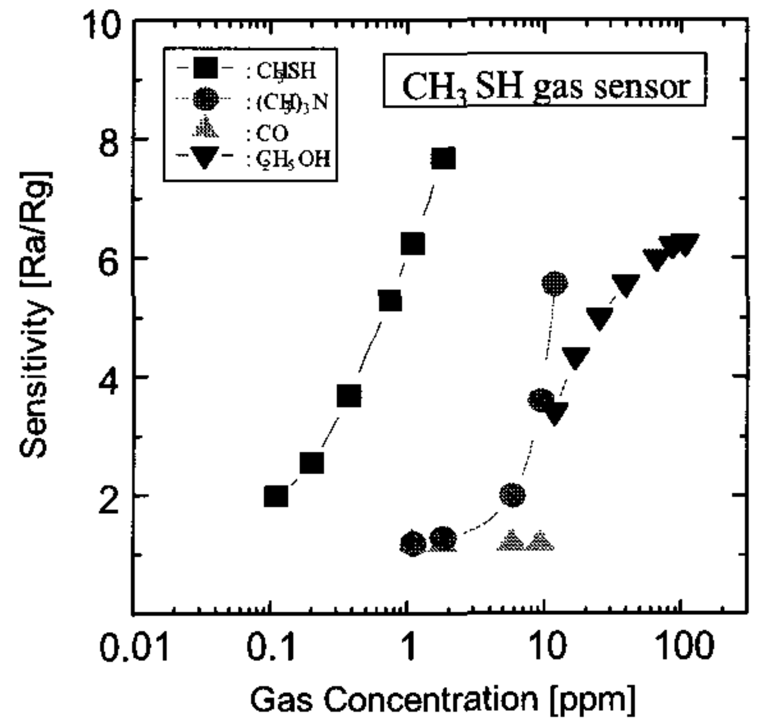

Fig. 5. Relationship between sensitivity and gas concentration for various gases.

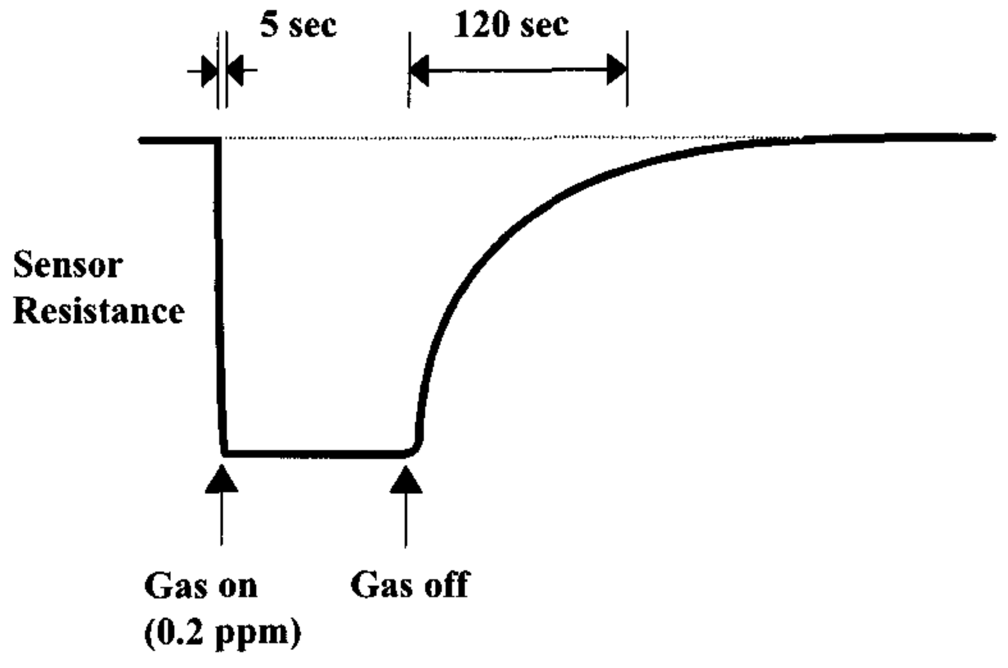

Fig. 6. Response to 0.2 ppm CH_3SH at 250°C.

The response time to the 0.2 ppm of CH_3SH is typically 5 sec (see Fig. 6). Fig. 7 shows the sensitivity versus $(CH_3)_3N$ concentration at the 4 different operating temperatures. The best results from the measurements of sensitivity and selectivity were obtained at 350°C.

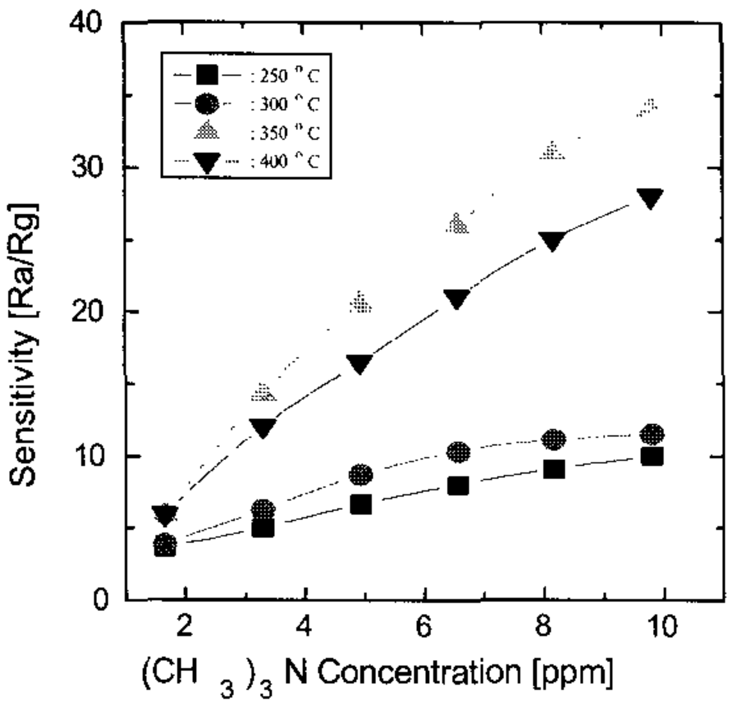

Fig. 7. Sensitivity vs. $(CH_3)_3N$ concentration at various operating temperatures.

Fig. 8 illustrates the selectivity to $(CH_3)_3N$ at 350°C. The Al_2O_3-doped ZnO sensor has, except for CH_3SH, good selectivity to $(CH_3)_3N$ in the ppm range. Fig. 9 represents a typical response curve of the sensor to 5 ppm of $(CH_3)_3N$ at 350°C. The response time of about 5 sec is at the same level as for the Pd-SnO_2 sensor to CH_3SH but the recovery time is much longer, which could be associated with the sticky characteristic of $(CH_3)_3N$ gas. The stability of the gas sensing layers was also examined. Fig. 10 shows the changes of output voltage(V_{out}) across the load resistance for 20 days, where the circuit voltage is 5V and the operating temperature is 300°C. From the results of the measurements, it is apparent that 3 days of aging process is necessary for the stable use of the gas sensing layers.

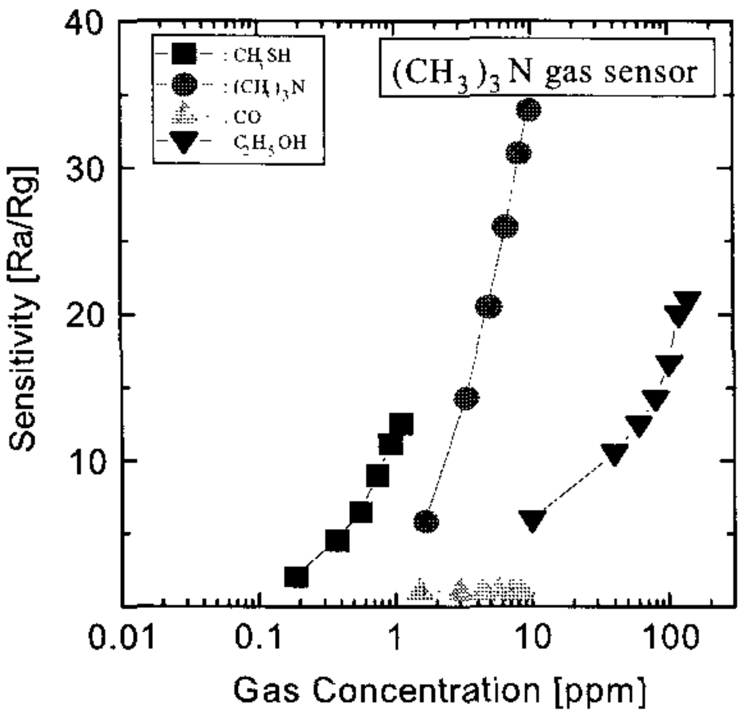

Fig. 8. Relationship between sensitivity and gas concentration for various gases.

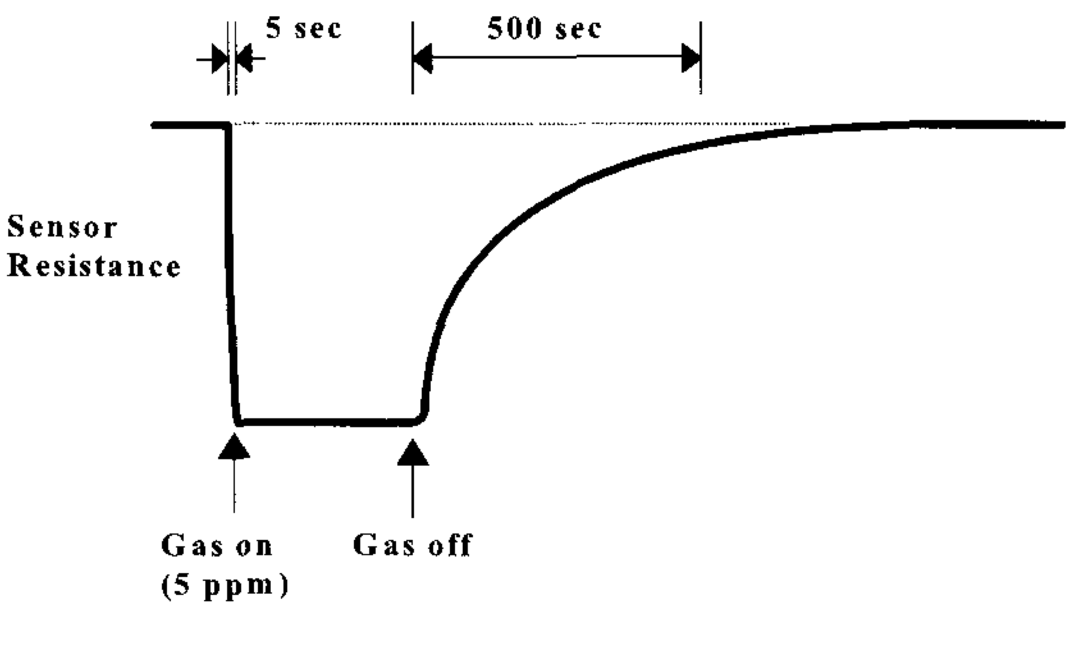

Fig. 9. Response to 5 ppm $(CH_3)_3N$ at 350°C.

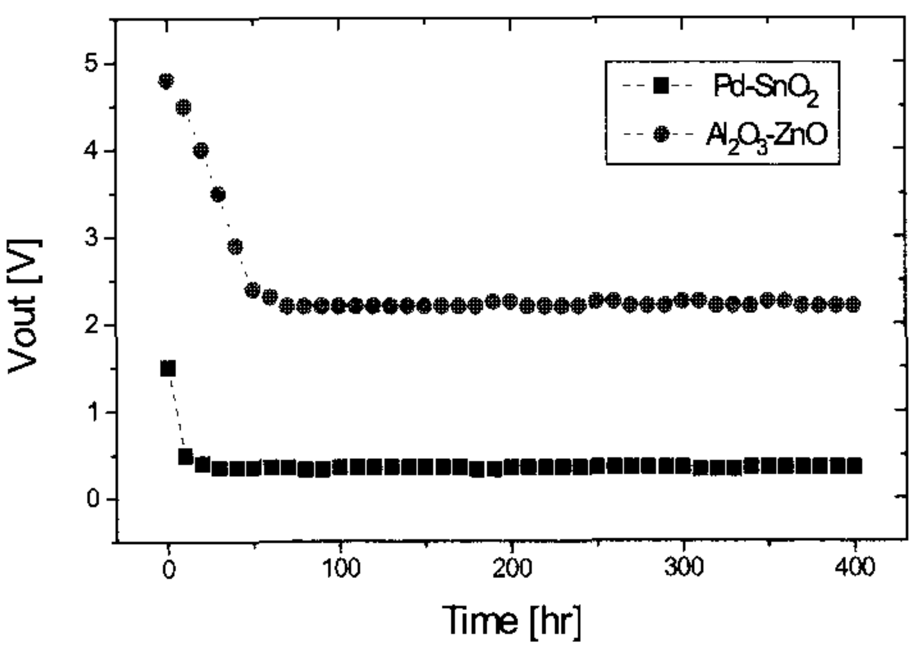

Fig. 10. Stability of the two sensing layers at the operating temperature of 300°C.

IV. CONCLUSION

Highly sensitive and mechanically stable micro-gas-sensors have been fabricated to detect CH_3SH and $(CH_3)_3N$. The sensing materials for CH_3SH and $(CH_3)_3N$ are 1 wt% Pd-doped SnO_2 and 6 wt% Al_2O_3-doped ZnO, respectively. Excellent thermal insulation is achieved using a double-layer membrane of 0.2μm-thick silicon nitride and 1.4μm-thick PSG. The heater made of Pt:4500Å/Ta:500Å consumes only 55mW and 85mW at the operating temperatures of 250°C and 350°C, respectively. The membrane is also mechanically stable enough to endure at least 43,200 heat cycles between room temperature and 350°C.

REFERENCES

[1] U. Dibbern, A Substrate for Thin-film Gas Sensors in Microelectronic Technology, *Sensors and Actuators B*, Vol. 2, pp. 63-70, 1990.

[2] P. Krebs and A. Grisel, A low power integrated catalytic gas sensor, *Sensors and Actuators B*, Vol. 13-14, pp. 155-158, 1993.

[3] W.Y. Chung, C.H. Shim, S.D. Choi and D.D. Lee, Tin oxide microsensor for LPG monitoring, *The 7th Int'nal Conf. on Solid-state Sensors and Actuators, Yokohama, 1993, pp. 428-431.*

[4] V.A. Zubstovsky, Y.M. Perov and Y.E. Sedakov, Design and manufacturing of gas sensors based on thin film semiconductors for oil and gas industries, *The 4th Int'nal Meeting on Chemical Sensors, Tokyo, 1992, pp. 320-321.*

[5] Q. Wu, K.M. Lee and C.C. Liu, Development of chemical sensors using microfabrication and micromachining techniques, *Sensors and Actuators B*, Vol. 13-14, pp. 1-6, 1993.

[6] V. Demarne and A. Grisel, An integrated low-power thin-film CO gas sensor on silicon, *Sensors and Actuators 13*, pp.301-313, 1988.

[7] V. Demarne and A. Grisel, A new SnO_2 low temperature deposition technique for integrated gas sensors, *Sensors and Actuators B*, Vol. 15-16, pp. 63-67, 1993.

[8] X. Wang, S. Yee and P. Carey, An integrated array of multiple thin-film metal oxide sensors for quantification of individual components in organic vapor mixtures, *Sensors and Actuators B,* Vol. 13-14, pp. 458-461, 1993.

[9] D. J. Smith, J. F. Vetelino and R. S. Falconer, Stability, sensitivity and selectivity of tungsten trioxide films for sensing applications, *Technical Digest of the 4th International Meeting on Chemical Sensors, 1992, pp. 312-315.*

[10] H. Nanto, H. Sokooshi and T. Usuda, Smell sensor using aluminium-doped zinc oxide thin film prepared by sputtering technique, *Sensors and Actuators B*, Vol. 10, pp. 79-83, 1993.

[11] Y. Takao, Y. Iwanaga, Y. Shimizu and M. Egashira, Trimethylamine-sensing mechanism of TiO_2-based sensors 1. Effect of metal additives on trimethylamine-sensing properties of TiO_2 sensors, *Sensors and Actuators B*, Vol. 10, pp. 229-234, 1993.

[12] I.-L. Kim, W.-B. Lee, J.-H. Cha and H.-D. Lee, Development of catalytic type gas sensor substrate by MEMS manufacturing process, *Proceedings of Korean Hydrogen and New Energy Society, 2004, pp. 661-665.*

[13] D. M. Byrne and S. Taguchi, The Taguchi approach to parameter design, *Quality Progress,* December, 1987, pp. 19-26.

Kyuchung Lee, Member KIMICS Received his B.S. degree in Electronic Engineering from Sungkyunkwan University in 1982, his M.S. degrees in Electronic Engineering from Yonsei University in 1984 and in Electrical Engineering from Georgia Institute of Technology in 1990, and his Ph.D. degree in IT Engineering from Mokwon University in 2003. From 1990 to 1998, he joined the LG Electronics Institute of Technology as a Senior Research Engineer. From 1998 to 2005, he was an assistant professor of the Department of Internet Information at Ajou Motor College. Since March 2005, he has been a non tenure-track professor of the Department of Information Technology at Sungkyul University. His research areas are Semiconductor gas sensors and Crystalline silicon solar cells.

Chang-Wu Hur, Member KIMICS Received his M.S. and Ph.D. degrees in Electrical and Electronic Engineering from the Yonsei University in 1984 and 1991, respectively. From 1986 to 1994, he joined at LG Research Center, where he worked as Senior Member of Technical Staff. In 1994, he joined the department of Electronic Engineering, Mokwon University, Korea, where he is presently a professor. His research interest is in the area of VLSI and Display that includes ASIC design, Display technology and Wireless communication design.