THIN FILM GAS SENSOR FOR DETECTION OF TOXIC GASES FROM MICROBIAL

Sang-Do Han[1], and Y.-S. Sohn[2]
[1]Korea Institute of Energy Research, Energy Conversion and Storage Research Center, Daejeon, 305-343, Korea
[2]Catholic University of Daegu, Gyeongsan-si, Gyeongbuk, 702-701 Korea

ABSTRACT

The metal-oxide semiconductor thin film gas sensor with high resistivity based on In_2O_3 has been characterized to detect toxic gases including acetaldehyde which stems from the mold. The sensor device was fabricated by coating of gold (Au) electrode and platinum (Pt) heater on the alumina substrate. In order to enhance the sensitivity the catalyst such as Au and palladium (Pd) was deposited using the thermal evaporator. The responses of the In_2O_3 metal-oxide semiconductor thin films with the Au catalyst show outstanding sensitivity, selectivity, absorption/desorption and linearity to acetaldehyde.

KEYWORDS

Sensor, toxic gas, thin film, Au catalyst

1. INTRODUCTION

The growth of the microbial VOCs (volatile organic compounds) leads to spoilage of food and animal feeds and to the formation of mycotoxins and potentially allergenic spores. Many researches have reported a relationship between those symptoms and the dampness and/or air contamination [1-3]. Microbial VOCs from mainly Aspergillus, Fusarium, and Penicillium have been characterized with gas chromatography, mass spectrometry, and sensory analysis. Common volatiles are 2-methyl-1-propanol, 3-methyl-1-butanol, 1-octen-3-ol, 3-octanone, 3-methylfuran, ethyl acetate, and the malodorous 2-methyl-isoborneol. Exposure of the sensor to volatile compounds gives rise to the changes in electrical quantities such as voltage shifts, change in resistance, or change in conductivity [4].

About 30,000-40,000 types of molds exist in the world, and it has been reported that about 200-300 types of molds are around the human life. These molds are well survived in temperature of 20-30 °C, humidity of 80-95%, and pH of 5.0-5.5, and water, carbon, nitrogen and oxygen are required as nutrients. The generated metabolic materials of the molds are CO_2, H_2O, CH_4, alcohols and small amount of mycotoxins. The diseases originated from these mycotoxins are ranging from dermatitis to cancer, and they will generate malfunction to human organs such as liver, lung, kidney, stomach, nerve and hematosis. The representative toxic gases generated from the mold are 2-methyl-1- propanol , 3-methyl-1-butanol), dimethyl disulfide, methyl sulfide, methyl mercaptane, acetaldehyde, and so on.

The performance test of the semiconductor-type gas sensors with detection range of 10 ppm to 100 ppm is required. By utilizing the phenomena of p/n-type semiconductor junction formation between particles, increase in absorption/desorption of the toxic gases and surface conduction of the nano-semiconductor material, many researches for thin film gas sensors to detect low concentration have been reported [5-11]. These sensors were based on the nano-sized catalysts deposited on the metal-oxide semiconductor thin film such as In_2O_3, SnO_2, WO_3, and TiO_2.

In this study, the metal-oxide semiconductor thin film was deposited on the alumina substrate, and the gas sensor was fabricated by coating of the precious metal catalyst on the sensing layer. The sensitivity and selectivity of the proposed sensor was investigated.

2. EXPERIMENT

Heater and electrode were screen-printed on the alumina substrate (4 × 3.5 × 0.25 mm^3). Heater and electrode were made of platinum and gold, respectively. They are formed on the front side of the alumina substrate. The space between electrodes was 320 μm. The schematic diagram of the sensing structure is shown in Figs. 1 and 2.

The screen mask for heat pattern was mesh 500 of SUS 304. To achieve 50 μm of the line space and less than 10 μm of film thickness, 24 μm thick mesh (first) and 3 μm thick emulsion (second) has been made.

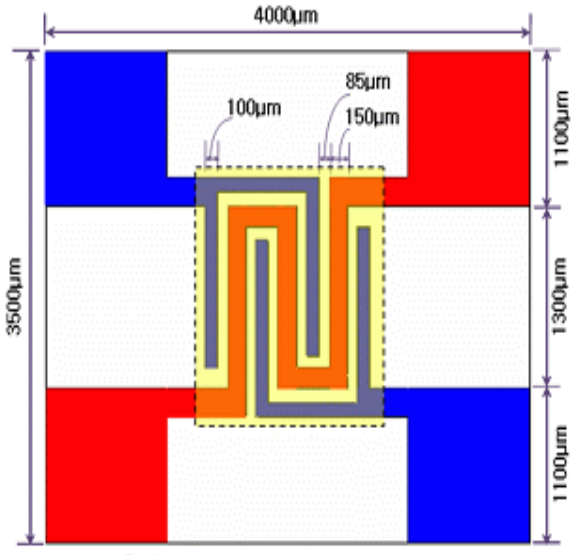

Figure 1: Schematic diagram of the sensor structure [Top view - red: heater; blue: electrode; yellow: sensing material (dot line)]

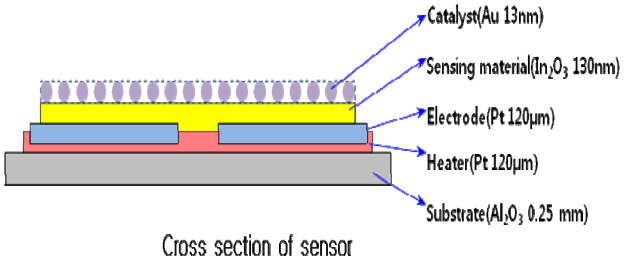

Figure 2: Schematic diagram of the sensor structure [Cross section view - red: heater; blue: electrode; yellow: sensing material]

Film thickness and uniformity depend on the viscosity of the sensing material. The viscosity of the paste used in this study was about 200 dPa·s. Through this process with high temperature heat treatment at 850 °C the gas sensor with Pt heater and electrodes was fabricated. Fig. 3 shows correlations of power consumption and temperature with the supplied voltage. About surface temperature of 300 °C was measured when 1.0 volt was applied.

Thin film of In_2O_3 sensing material was deposited using Ion Beam Sputter (IBS). The deposition condition is shown in Table 1. The initial vacuum pressure was 1×10^{-6} torr, and the deposition pressure was 3×10^{-5} torr. The sputtered thin film was heat-treated at 800°C. A thin Au-catalyst was deposited on the In_2O_3 sensing material by thermal evaporator. The fabricated thin film was investigated by scanning electron microscope (SEM), and the response of the sensor to the similar toxic gases were measured and analyzed. In this study, Agilent 34907A has been used to measure the resistance change accurately. The sensing and catalyst materials have the purity of 99.9 %.

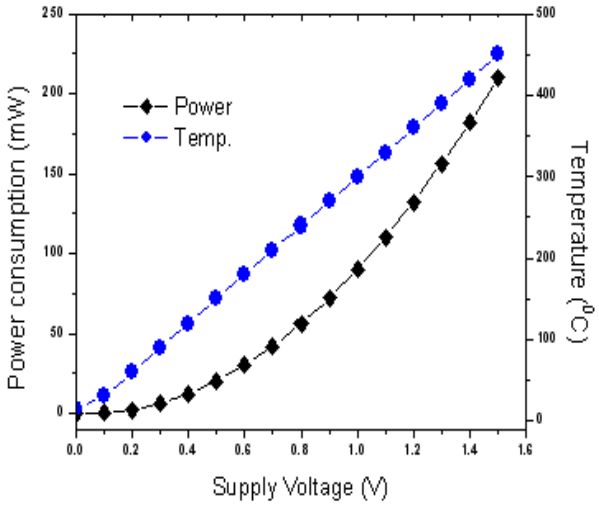

Figure 3: Correlation of power consumption and temperature with supplied voltage

Table 1. Deposition condition of In_2O_3 material

In_2O_3 sputtering (40min)			
Rotation	5	HV	8kV
Title angle [Deg]	30	Current	3mA/Gun
Tile speed	5	Vacuum	3×10^{-5} torr

3. RESULTS AND DISCUSSION

Fig. 4 shows the SEM image of the prepared homogeneous In_2O_3 sensing layer. Our optimized deposition time was 40 min. The reason is that when the deposition time was 20 min the film was too thin so that it was very difficult to measure the resistance, and when the deposition time was 60 min the film was too thick to get the high sensitivity. When the deposition time was 40 min, the thickness of the film was 120 – 143 nm as shown in Fig. 4. The resistivity of the sensing layer is about 155 kΩ. Au granules as catalytic materials were deposited on the In_2O_3 sensing layer using thermal evaporator, as shown in

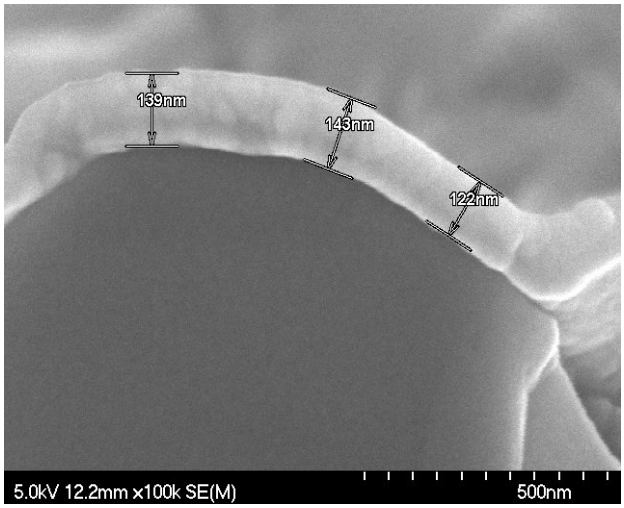

Figure 4: SEM image of In_2O_3 thin film

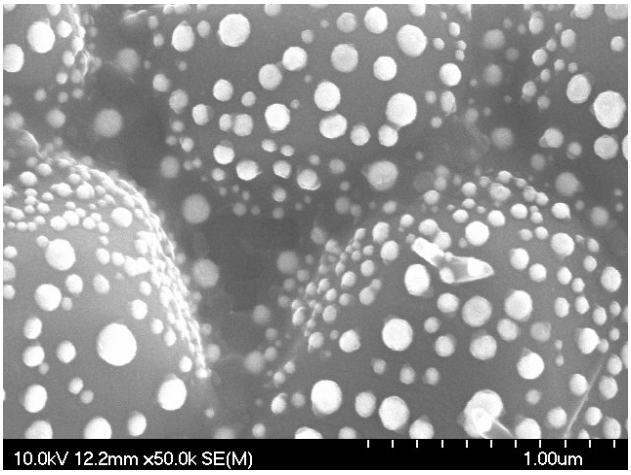

Figure 5: SEM image of Au particles deposited on the In_2O_3 thin film

Fig. 5. The small amount of the Au granule with size of 30-100 nm in diameter as well as homogeneous distribution could play a role as the catalyst. It is expected that Au catalyst enhances the sensitivity of the sensor. After thermal treatment the sensor was connected to the packaging body using Pt wire by micro spot welder (Spot Welder:TITH Corporation, WMH-V1). The packaged sensor is shown in Fig. 6.

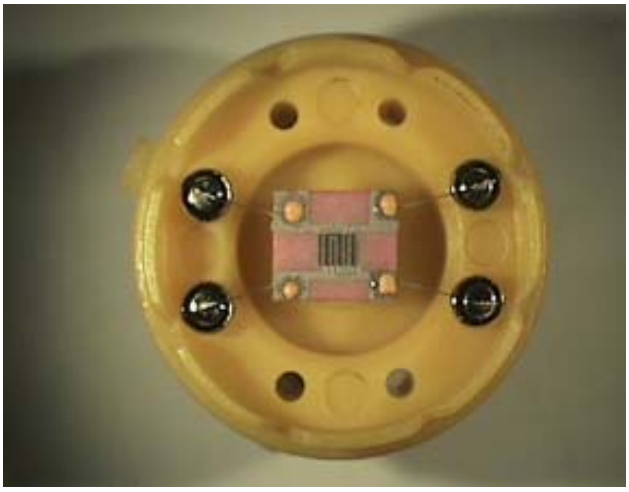

Figure 6. Packaged device with Pt wire

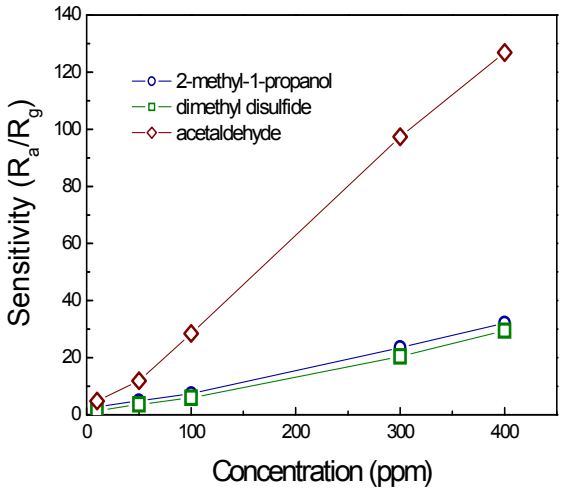

Figure 7. Sensitivity of In_2O_3-Au nanocrystalline film with respect to concentration of three different gases

Fig. 7 represents the sensitivity and selectivity of the device when it is exposed to 2-methy1-1-propanol ($C_4H_{10}O$), acetaldehyde (C_2H_4O) and dimethyl disulfide ($C_2H_6S_2$) with different concentration. We affirmed that the sensor showed linearity to each gas as shown in Fig. 7. The fixed temperature (250°C) during gas sensing experiments is necessary as the sensitivities of In_2O_3 based sensors to specific gases are dependent on concentrations. It may be observed from Fig. 7 the sensor showed weak response to 2-methy1-1-propanol and dimethyl disulfide throughout the operating temperature at 250°C. In case of acetaldehyde, the sensitivity is the highest among the gases, and its value to the minimum concentration(10 ppm) was 4.8 at temperature of 250°C. The response of the sensor to acetaldehyde with concentration of 100 ppm is shown in Fig. 8. A large difference in resistance from about 155 kΩ to 100 kΩ, fast response of absorption and desorption, retrieval of its initial resistance level revealed its superiority.

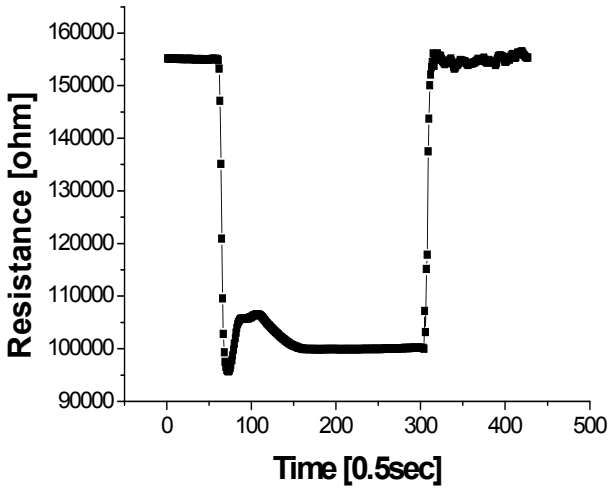

Figure 8. Sensitivity of In_2O_3-Au nanocrystalline film with respect to concentration of three different gases

4. CONCLUSION

A high-performance acetaldehyde gas sensor with In_2O_3-Au nanocrystalline sensing layer has been designed, fabricated and characterized. The response of the proposed sensor was investigated with respect to acetaldehyde that is known as one of the microbial VOCs. The sensitivity of the sensor device under different concentrations and temperatures has been observed. The sensor showed higher response and good sensitivity to this gas at 250°C. The minimum concentration of the acetaldehyde that can be detected is 10 ppm. The investigated results are satisfactory in sensitivity, absorption/desorption, reproducibility, stability and linearity of the output signal. Detection of ultra-low concentration less than 10 ppm and field test were experiments worth trying. The proposed sensor would be a promising practical device for the low concentration microbial VOCs gas detection.

REFERENCES

[1] G.H. Wang, C.S. Li, “Indoor endotoxin and glucan in association with airway inflammation and systemic symptoms”, Arch. Environ. Health, Vol. 54, pp. 172–179, 1999.

[2] O. Koskinen, T. Husman, A. Hyvärinen, T. Reponen, A. Nevalainen, “Two moldy day-care centers: a follow-up study of respiratory symptoms and infections”, Indoor Air, Vol. 7, pp. 67–76, 1997.

[3] D. Norback, G. Wieslander, K. Nordstrom, R. Walinder, “Asthma symptoms in relation to measured building dampness in upper concrete floor construction, and 2-ethyl-1-hexanol in indoor air”, Int. J. Tuberc. Lung Dis., Vol. 4, pp. 1016–1025, 2000.

[4] Dickinson, T. A., White, J., Kauer, J. S., and Walt, D. R., “Current trends in “artificial-nose” technology”, Trends Biotech., Vol. 16, pp. 250–258, 1998.

[5] J. Olsson, T. Borjesson, T. Lundstedt, J. Schnurer, Volatiles for mycological quality grading of barley grains: determinations using gas chromatography–-mass spectrometry and electronic nose, Int. J. Food Microbiol., Vol.59, pp. 167–178, 2000.

[6] D. Tuma, R.N. Sinha, W.E. Muir, D. Abramson, Odor volatiles associated with microflora in damp ventilated and non-ventilated bin-stored bulk wheat, Int. J. Food Microbiol., Vol. 8, pp103–119, 1998.

[7] M. Kuske, R. Rubio, A.C. Romain, J. Nicolas, S. Marco, "Fuzzy k-NN applied to moulds detection", Sensors and Actuators B, Vol.106, pp. 52-60 2005.

[8] M. Kuske, M. Padilla, A.C. Romain, J. Nicolas, R. Rubio, S. Marco, "Detection of diverse mould species growing on building materials by gas sensor arrays and pattern recognition", Sensors and Actuators B, Vol. 119, pp. 33-40, 2006 .

[9] Chi-Hwan Han, Il-Jin Kim, Won-Bae Lee, and Sang-Do Han, “Hydrogen sensitive micro sensor of nano-crystalline F-doped SnO_2 using MEMS technology”, *The 10th International meeting on Chemical Sensors, Tsukuba, Japan*, July 11-14, 2004 pp.694-695

[10] Sang-Do Han, “R and D of Chemical Sensor for Mold Detection in Living Environment”, Technical Report, Korea Institute of Energy Research, 2008

[11] G. Korotcenkov, S.-D. Han, B.K. Cho and V. Brinzari, “Grain Size Effects in Sensor Response of nanostructured SnO2- and In2O3-based Conductometeric Thin Film Gas Sensor”, Critical Reviews in Solid State and Materials Sciences, Vol.34, pp. 1-17, 2009

CONTACT

* Sang-Do Han, Tel: 82-42-860-3449; sdhan@kier.re.kr