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Detection of Blood Agent Gas Using SnO_2 Thin Film Gas Sensor

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Abstract

In this study, thin film gas sensor based on tin oxide was fabricated to examine its characteristics. Target gas is acetonitrile (CH_3CN) which is a blood simulant for the chemical warfare agent. Sensing materials are SnO_2, SnO_2/Pt, and Sn/Pt with thickness from 1000 to 3000 Å. The sensor consists of a sensing electrode with inter-digit (IDT) type in front side and a heater in rear side. Resistance changes of sensing materials are monitored on real time basis using a data acquisition board with a 12-bit analog to digital converter. Sensitivities are measured at different operating temperatures also with different gas concentrations and film thickness. The high sensitivity is obtained for Sn (3000 Å)/Pt (30 Å) at 300°C for 3 ppm. Response and recovery times were about 40 and 160 s, respectively. Repetition measurements showed very good results with ±3% in full scale range.

Key words : SnO_2, Thin film, CH_3CN, Blood agent gas

1. INTRODUCTION

Major advances have occurred in the past few years in our understanding for the mode of action of the classical, biological and chemical warfare agents and in their treatment (Marrs *et al.*, 1996). Especially, chemical warfare agents (CWAs) are very dangerous because of their colorlessness and toxicity. Therefore, fast and correct detection of CWA is essential to protect human beings. CWAs are very harmful gases that gave human being a mortal wound with a small amount. They are divided into four types such as blood, nerve, vesicant, and choking agent (Lee, 1999). Comparison of data between nuclear weapon (one of the most dangerous weapons in the world) and chemical weapon was shown in Table 1. In the direct effect range, they have similar range and casualties, too. Especially, the production cost of chemical weapon is very low at the most 1 : 100, and very difficult to detect comparing the nuclear weapon.

We used tin oxide based gas sensors to detect various CWAs. Gas sensors that can detect trace amounts of gases are used in the chemical and pharmaceutical industries to control the amount of harmful wastes, possible explosion of combustible gases, incomplete combustion of exhaust gases from automobiles and clinical testing. Such sensors show many advantages over optical or electrochemical sensors. The main advantages are low cost, low consumption of electrical power, and high sensi-

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Table 1. The comparison between nuclear weapon and chemical weapon.

Contents	Nuclear weapon	Chemical weapon
Direct effect range (km^2)	190-260	260
Remaining effect	6 months	3-36 hrs
Casualties	98% dead	30% casualties
Response time of effect	A few sec.	7 sec-30 min
Product cost ($/ton)	1,000,000	10,000
Identification of detection	Simple	Complex

tivity (Sohn *et al.*, 2000).

Categories of the semiconductor gas sensor are divided into thick films and thin films (Lee *et al.*, 2003; Chung, 2002). Generally, the former shows high sensitivity at low level concentration but has stability problem (Choi *et al.*, 2002; Lee *et al.*, 2000; Lee and Lee, 1999). The latter has high stability and repeatability but lower sensitivity (Kim and Song, 1995; Shin and Kim, 1995).

Thin film gas sensors are fabricated to detect acetonitrile gas that is simulant gas of blood agent (Choi *et al.*, 2003; Marrs, 1996; Park, 1992). Materials were characterized by XRD and SEM analysis and gas response characteristics was tested to simulant gas.

2. EXPERIMENTS

2.1 Fabrication of Gas Sensing Device

Fig. 1 shows the fabrication process of a thin film gas sensor. Pt for sensing electrode was deposited 1000 Å thickness using a DC sputter at the front side of alumina substrate and an electrode for the heater was screened using a Pt paste at the back side of it. Then the device was thermally annealed at 850°C for 10 min in the electric furnace. The resistance of a heater was 10 ohms. Sensing films were configurated as three types as shown in Fig. 1. At first, all three sensing films were deposited from 1000 to 3000 Å thickness to examine gas response characteristics using the thermal evaporator. In the case of Fig. 1(a), deposited Sn was thermally oxidized at 700°C for 10 hr in the O_2 atmosphere. In the case of Fig. 1(b), after oxidation process, sensor was added 30 Å thickness of Pt using the ion coater. And then sensor was conducted thermal process at 600°C for 1 hr in N_2 atmosphere. In the case of Fig. 1(c), after adding Pt sensor was thermally oxidized at 700°C for 10 h in the O_2 atmosphere to block Sn particles growth (Shim *et al.*, 2002). All the complete sensors were tested after aging at 400°C for 3

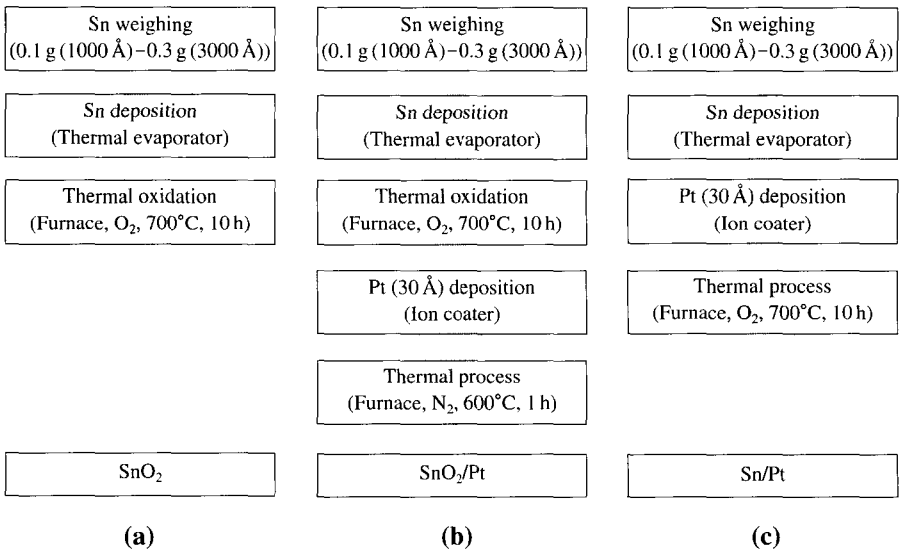

Fig. 1. The fabrication process of a sensor.

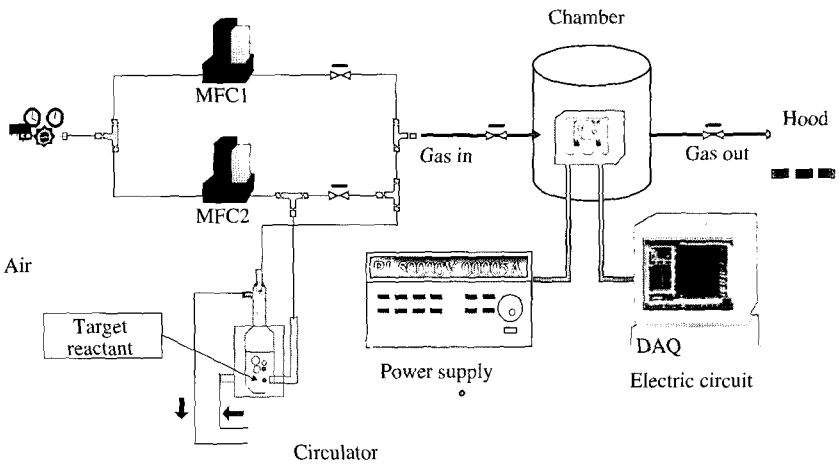

Fig. 2. Measurement apparatus.

days. Total dimension of device was 7 mm × 10 mm × 0.6 mm and the size of sensing film was 6 mm × 4 mm.

2.2 Apparatus and Measurement Method

Apparatus of experimental measurement was shown in Fig. 2. Acetonitrile (CH_3CN) is used as a test gas. Acetonitrile has 41.05 molecular weight and is a liquid at room temperature. Reaction between acetonitrile and SnO_2 surface was shown in Equation 1 (Park, 1992). It has been reported that CH_3CN undergoes oxidation reaction giving product of ammonia and carbon dioxide.

$$CH_3CN+2O_2 \rightarrow NH_3+2CO_2 \quad (1)$$

Vapor pressure of acetonitrile can be calculated using the Equation 2 from liquid pahse. Equation 2 is Antoine equation that can calculate vapor pressure of liquid phase at specific temperature. Using this equation, vapor of liquid is calculated and then measurement gas concentration can change by using dilution with air. Gas amounts are controlled by using two mass flow controllers (MFCs). Gas concentration is controlled in the chamber using air through no. 1 MFC and vapor of real acetonitrile. Total mass flow is fixed 1000 ml/min.

Used equation is as follows

$$\log_{10}P = A - \frac{B}{(T+C)} \quad (2)$$

where, P(bar) means vapor pressure, constant A, B, C were 5.93296, 2345.829 and 43.815, respectively. And T(K) means temperature of saturator. As you see in Equation 2, gas concentration can be controlled by using the saturator temperature. Saturator of Fig. 2 has acetonitrile (Aldrich, 99.8%) liquid and correct saturator temperature was controlled by a circulator. Change of sensing film resistance is acquired using data acquisition (DAQ) board (E6024 NI co., USA.) (Kwak, 2002). Used DAQ board can acquire simultaneous 16 channels of analog input and 500,000 samples per 1 sec.

3. RESULTS AND DISCUSSION

3.1 Characteristics of Sensing Materials

Fabricated sensors were analyzed by the scanning electron microscopy (SEM) for surface morphology and thickness and by X-ray diffractometer (XRD) for the characterization of the thin film. SEM photograph of a sensor that was deposited with Sn 0.1 g is shown in Fig. 3. Fig. 3(a) and (c) are Sn top view

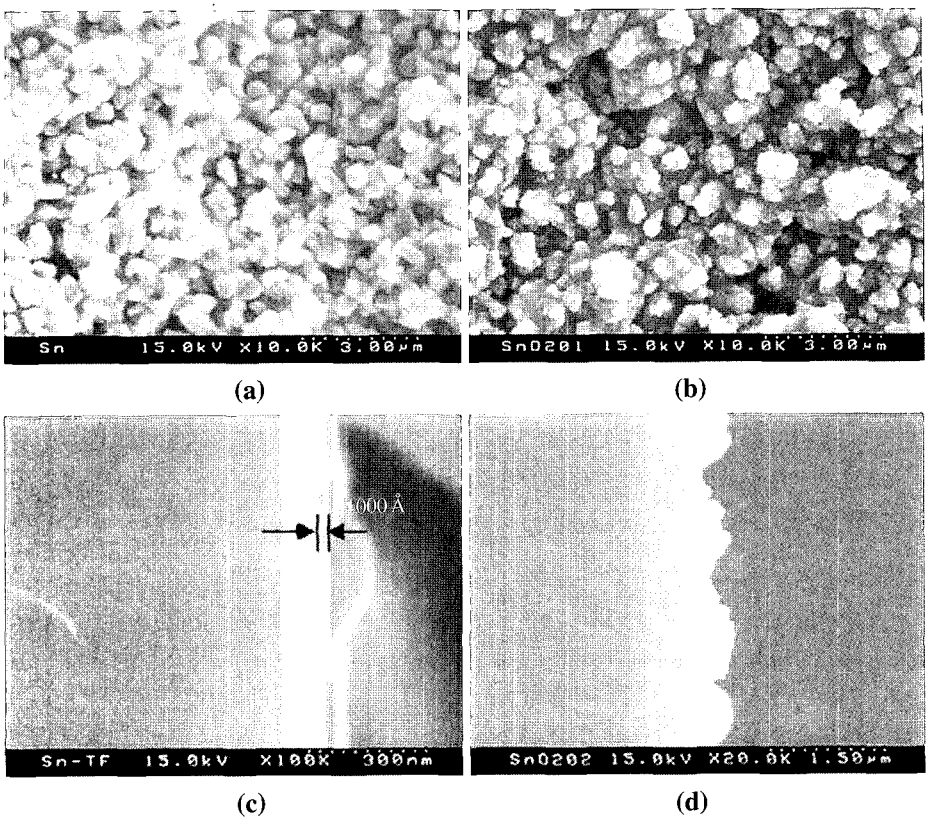

Fig. 3. SEM photograph of SnO_2 thin film. (a) Top view (c) cross sectional view of before thermal treatment (b) top view (d) cross sectional view of after thermal treatment.

and cross sectional view photograph before thermal oxidation and Fig. 3(b) and (d) are SnO_2 top and cross sectional view photograph after thermal oxidation. As shown in Fig. 3, Sn is deposited 1000 Å thickness at surface and in Fig. 3(d) SnO_2 is agglomerated after thermal oxidation.

3.2 Temp. vs. Resistance Property of Fabricated Sensing Materials

Fig. 4 shows the resistance characteristics with different operating temperatures and with different film thickness of sensing materials. Resistance property was very important to select operating temperature of the sensor. Generally, operating temperature is selected as temperature range that has comparatively small resistance change because resistance has very small change through large

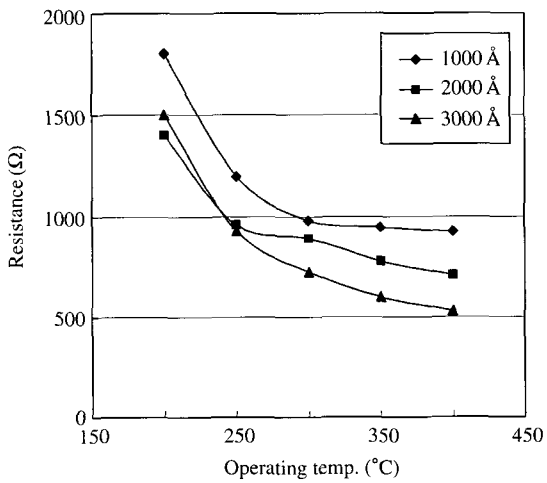

Fig. 4. Resistance vs operating temp. as sensing film thickness.

temperature change results from environment change. As shown in Fig. 4, the range of over 250°C has a little resistance change and 1000 Å thickness sensor was shown very little resistance change over 300°C. So, the operating temperature was selected from 250 to 350°C.

3.3 Response of Test Gas

Response properties were measured for test gases. Measurement were performed on sensing film thickness with 1000, 2000, and 3000 Å, operating temperature with 250, 300, and 350°C and CH_3CN concentration from 0 to 10 ppm. The effect for sensing film thickness was measured from 1000 to 3000 Å as shown in Fig. 5. CH_3CN concentration of 3 ppm and operating temperature 300°C were fixed in this experiment. The definition of sensitivity is shown in Equation 3.

$$S(\%) = \frac{R_g - R_a}{R_a} \times 100 \quad (3)$$

In which, Ra and Rg mean resistance of air atmosphere and gas atmosphere, respectively. For example, if Ra and Rg are 500, 250 kΩ respectively, sensitivity is −50%. Negative value means that the resistance of sensor will decrease after action between sensing material and gas. In other words, Rg is smaller than Ra. The sensing materials with 3000 Å thickness showed good sensitivity and Sn/Pt showed better sensing behaviour. From the above results, it was found that Pt catalyst affected the sensitivity to a great extent. Optimum sensing film thickness was found to be 3000 Å for good sensitivity.

Fig. 6 shows response property with operating temperatures. CH_3CN concentration 3 ppm and sensing film thickness 3000 Å were fixed in this experiment. As shown in Fig. 6, it is observed that the operating temperature 300°C showed high sensitivity in comparison to other temperatures. In general, when operating temperature goes up, gas absorption and desorption on the surface is fast. So, adsorption is faster than desorption under specific temperature (in case of this study, specific temperature means 300°C) but desorption is faster than adsorption over specific temperature.

Fig. 7 shows a sensitivity graph as CH_3CN concentration change with sensing film thickness 3000

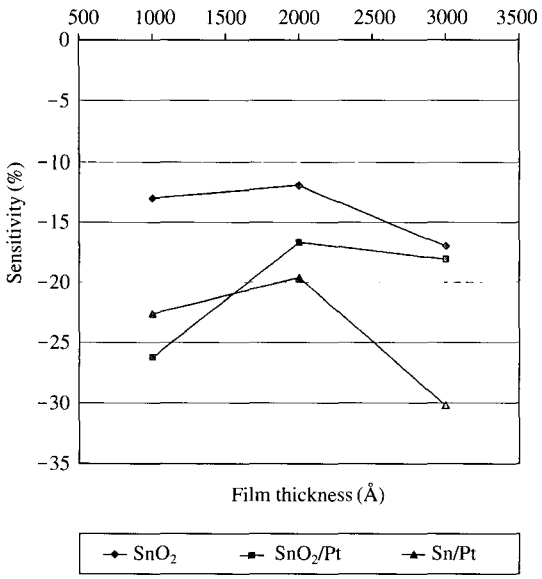

Fig. 5. Sensitivity as sensing film thickness (CH_3CN : 3 ppm, Operating temp. : 300°C).

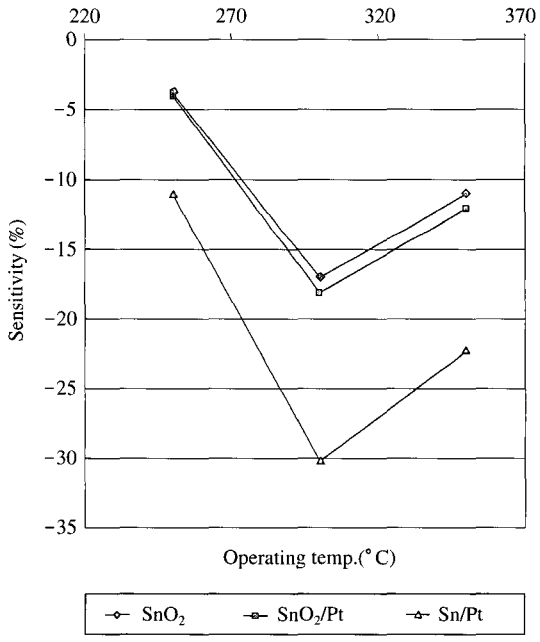

Fig. 6. Sensitivity with the operating temperature (CH_3CN: 3 ppm, thickness: 30000Å).

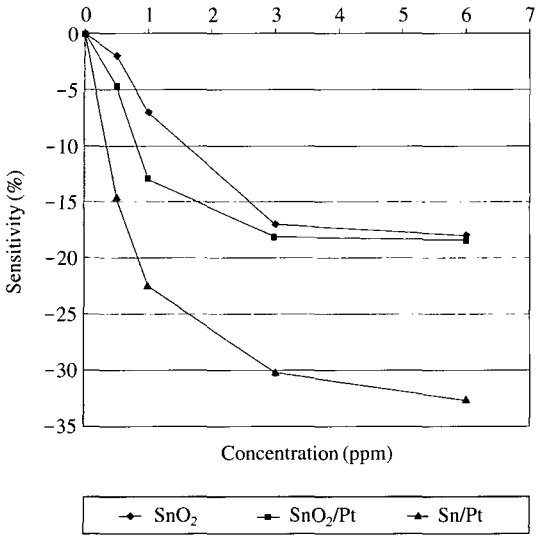

Fig. 7. Sensitivity with CH_3CN concentration.

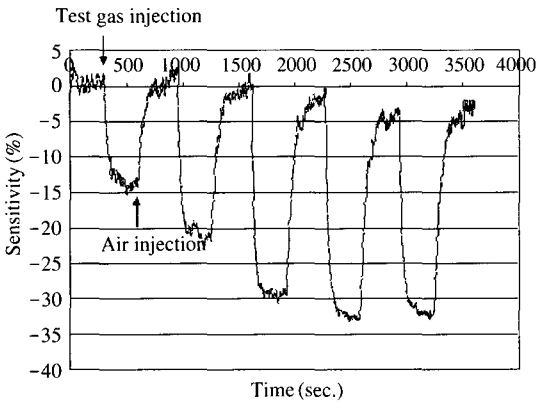

Fig. 8. Real time response curve as CH_3CN concentration.

Å. By 3 ppm of CH_3CN concentration, sensitivity linearly decreases, but over 3 ppm of CH_3CN concentration, the change is very small. This results from limitation of gas reaction site on sensor surface. So, sensitivity increase in low concentration because sensor surface has many reaction sites. But sensitivity is saturated in high concentration because many sites already reacted between gas and sensing material.

Fig. 8 shows a real time response graph by the PC

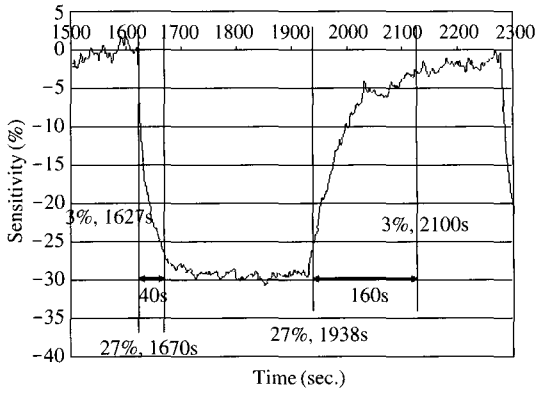

Fig. 9. Response time and recovery time graph.

output with CH_3CN concentrations. Sensing film Sn/Pt, thickness 3000 Å and operating temperature 300°C were fixed in this experiment. After stabilizing for 3 min, measurement gas was injected for 5 min and followed by fresh air was injected 5 min using the MFC respectively. Injected concentrations were 0.5, 1, 3, 6, 6 ppm by turns. For the repetition test, concentration 6 ppm was injected two times. As shown in Figure, at first sensitivity presented 33%, at second presented 32%. The error between two values was below ±3% in full scale.

Fig. 9 shows a response and recovery time graph. Response time is generally defined as rising time from 10 to 90% of saturation value and recovery time was reverse of response time (Lee, 2001). The measurement results of response time and recovery time were shown about 40 s (from 1627 to 1670) and 160 s (from 1938 to 2100) respectively. But, the real response time will be shorter than 40 s because fabricated system was gas flow system using the MFC, so diffusion time from gas cylinder to measurement chamber is required.

4. CONCLUSIONS

A CH_3CN gas sensor based on tin oxide was fabricated and gas response characteristics were examined with sensing film thickness ranging from 1000 to 3000 Å, with operating temperature from 250 to

350°C, with CH_3CN concentration from 0 to 10 ppm. 3 ppm concentration of CH_3CN showed 30% sensitivity at 300°C with Sn/Pt 3000 Å film thickness. Response time and recovery time were 40 s and 160 s respectively and the repetition test was excellent ± 3% in full scale. These samples may be applicable sensors and can be exploited as commercial sensors.

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