NO\textsubscript{x} gas response characteristics of thin film mixed oxide semiconductor

Kap-Duk Song\textsuperscript{a}, Jung-Il Bang\textsuperscript{a}, Sang-Rok Lee\textsuperscript{a}, Yun-Su Lee\textsuperscript{a}, Young-Ho Hong\textsuperscript{b}, Duk-Dong Lee\textsuperscript{a,}\textsuperscript{*}

\textsuperscript{a} School of Electronic and Electrical Engineering, Kyungpook National University, 1370 Sankeokdong, Bukgu, Daegu 702-701, Republic of Korea
\textsuperscript{b} School of Digital Electronic Engineering, Kyungwoon University, Gumi 730-850, Republic of Korea

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Abstract

Many metal oxide gas sensors have been developed for improving stability during last several decades. In this paper, we proposed the hot-wire type micro-gas sensor with single electrode for improving sensitivity and stability. This type sensor has only a single electrode by forming a sensing material onto Pt heater so the resistance of the single electrode is very low for parallel values of Pt heater resistor and sensing materials of mixed oxide semiconductor. Mixed oxide (Sn–In)O\textsubscript{2}+Pt with various composition Sn–In = 1:1, 2:1, 5:1 and 10:1 for sensing materials were prepared. The fabricated sensor showed high sensitivity for NO\textsubscript{x} at low gas concentration and good selectivity for CO and HC gases.

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1. Introduction

Widely used gas sensor types in house and workplace are semiconductor type and catalytic type. In general, semiconductor gas sensor has good merits in sensitivity. But semiconductor gas sensor has a disadvantage in structure with isolation of heater and sensing material. Semiconductor gas sensors based on SnO\textsubscript{2} or other materials have been studied for detection inflammable or toxic gases. However, the lack of stability is one of the disadvantages. Catalytic gas sensor has a simple structure in contrast with low sensitivity at low gas concentration and poor long-term stability. And the other serious problems of catalytic type gas sensor are heat loss and poisoning. In order to minimize heat loss, low thermal conductivity material and thermally isolated device structure should be required. Poisoning effect occurs when there are strong absorptions of Si vapor, phosphate esters and sulfur containing compounds. And it induces the loss of sensitivity because the strongly adsorbed gases pre-occupy catalyst sites and inhibits catalytic reaction between catalyst and detecting gases [1–4]. In order to overcome these disadvantages of these gas sensors, it could be good methods for gas sensor to have sensing material of n-type semiconductor material and structure of catalytic gas sensor. Despite high sensitivity of the gas sensors could be obtained by adding additives such as Pt, Pd, Ag, etc., it might not be guaranteed high stability [5,6]. High stable gas sensor means that it does not have drift of sensor output signal in a normal air condition and have a good reproducibility.

In the previous work, it was found that this structure (i.e. hot-wire sensor [7]) with SnO\textsubscript{2}+Pt sensing material could be a good candidate [8]. That sensor showed a high sensitivity for CO gas over 500ppm and a little drift at normal air ambient. Therefore, this study has been focused on sensor fabrication with better sensitivity for NO\textsubscript{x} gas at low concentrations.
gas concentration, advanced long-term stability. Mixed oxide semiconductor (Sn–In)O + Pt was a good candidates for sensing material for NO\textsubscript{x} gas at low concentration.

2. Experimental

2.1. Fabrication of sensor device

Various compositions of (Sn–In)O thin film were deposited with its thickness 2000 Å on pyrex 7740 substrate. The deposited films were annealed at 600 °C for 3 h in O\textsubscript{2} ambient. And then Pt 40 Å was added for catalyst. Five types of sensing material were prepared as the Sn–In ratio were from 0 to 10. In order to fabricate thin film micro-gas sensor, two masks were needed for lithography process. First mask (mask #1) was for the heater etching process of Pt heater. Second mask (mask #2) was for lift off process of sensing film. The designed device size was 2 mm \times 2 mm. The line width of heater was 20 μm.

Fig. 1 shows process sequence of the sensor fabrication. Fabricated device was no deteriorations under long-term usage and showed a good rigidity to physical stress because 125 μm thick glass (pyrex 7740) was used as a substrate of sensor.

2.2. Measuring and detecting of sensing signal

Fig. 2 shows the equivalent circuit for the operation of this sensor. At the gas exposure, the sensor output was obtained as a voltage change \( \Delta V_o \). The resistance of RMO in a single electrode was decreased according as reducing gas concentration is increased, so \( V_o \) was increased and vice versa.

In order to extract the sensing signals, we used a simple method of measuring output voltages because this fabricated gas sensor had high output voltage in contrast to catalytic gas sensors.

3. Results and discussions

As the results of the previous works [7], it was found that the resistance of sensing material should be some low for good sensitivity. Therefore, it was prepared (Sn–In)O + Pt sensing material. As increased indium quantities, RMO was decreased in some extents. Fig. 3 shows temperature dependence of sensor resistance of (Sn–In)O + Pt element, RMOs for various component of Sn. RMO was decreased in some extents. But the RMO of (Sn–In)O + Pt was much lower than that of (Sn–O) + Pt. Therefore, the fabricated sensor has a chance to be high sensitive.
Fig. 3. Temperature dependence of sensor resistance of (Sn–In)O + Pt element, RM0s for various component of Sn.

Fig. 4 shows the SEM photographs of the (Sn–In)O + Pt thin films. As shown in Fig. 4, in case of the ratio Sn–In = 5:1, the grain boundary was clearly appeared and the grain size was about 100 Å.

To investigate the gas response of this fabricated sensor, four types of gases (NO\textsubscript{x}: 0.5–10 ppm; CO, C\textsubscript{4}H\textsubscript{10}, and C\textsubscript{2}H\textsubscript{5}OH: 50–2000 ppm) were injected to test chamber (10 L). The applied power variations were from 200 to 350 mW with steps 50 mW. Fig. 5 shows the gas responses of the five types prepared sensor elements as various power consumptions of 200, 250, 300, and 350 mW. As shown in Fig. 5, in case of Sn–In = 5:1, the $\Delta V_o$ (sensitivity) was the highest. Overall, the fabricated sensors show good sensitivities except Sn–In = 1:1. In the next Fig. 6, it was shown that NO\textsubscript{x} gas responses of Sn–In = 5:1, according to the applied power. According as the applied power was increased to 350 mW, $V_o$ was decreased linearly as a function of gas concentration.

Fig. 4. SEM photographs of sensing materials annealed at 650 °C: (a) Sn–In = 1:1; (b) Sn–In = 2:1; (c) Sn–In = 5:1; (d) Sn–In = 10:1.

Fig. 5. NO\textsubscript{x} gas responses of the five types prepared sensor elements as various power consumptions of 200, 250, 300, and 350 mW.

Fig. 6. NO\textsubscript{x} gas responses of Sn–In = 5:1 according to the applied power.
\( \Delta V_o \) was about \(-200 \) mV for 5 ppm NO\(_x\) gas at 250 mW. But the increasing rate of \( \Delta V_o \) over 300 mW was rather decreased because of the saturation of sensing material for NO\(_x\) gas. In case of under 1 ppm of NO\(_x\) gas concentration, the slope of the \( \Delta V_o \) as a function of gas concentration was much linear rather than high NO\(_x\) gas concentrations. However, overall slope of \( \Delta V_o \) as a function of gas concentration was linear in contrast with general semiconductor type gas sensors. The characteristics of general semiconductor type gas sensor show that it can be difficult to differentiate gas concentrations from the sensor characteristics as gas concentration goes to high. However, the obtained characteristics of this fabricated sensor were very similar to those of catalytic type gas sensor different from semiconductor type gas sensor. In a view of sensitivity, the output voltage of fabricated sensor had much higher than that of catalytic type gas sensor.

Fig. 7 shows NO\(_x\) gas response curve of Sn–In = 5:1 sensor at 250 mW. It can be seen that high response time and typical NO\(_x\) gas recovery characteristic is shown. Unlike, the characteristics of NO\(_x\) gas response, as the CO, hydrocarbon (HC) and alcohol gases concentration was increased, the \( \Delta V_o \) was increased at the same time. In Fig. 8, it shows various gas responses according to the applied power for Sn–In = 5:1 (NO\(_x\): 10 ppm; CO, C\(_4\)H\(_10\), and C\(_2\)H\(_5\)OH: 1000 ppm). The \( \Delta V_o \) are dozens of mV for these other gases for 1000 ppm and showed rather good selectivity to these other gases.

4. Conclusion

We propose new type of micro-hot-wire gas sensor with single electrode for improving sensitivity for NO\(_x\) gas. Fabricated sensor has only a single electrode by forming a sensing material of (Sn–In)O + Pt onto Pt heating electrode. Thus, this fabricated micro-gas sensor shows low resistance, therefore also the sensor output signal could be stabilized for abrupt temperature changes. As a result of NO\(_x\) gas sensing characteristics, this fabricated sensor shows \(-300 \) mV sensitivity for 20 ppm and has linearity for wide range (0.5–20 ppm) of gas concentration. And the sensor shows a good recovery characteristic of \( \pm 5 \) mV deviation compared to initial voltage output.

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References


Biographies

Kap-Duk Song received the BS and MS degrees in engineering from Kyungpook National University in 1994 and 1996, respectively. Currently, he is enrolled in a doctoral course at the School of Electronic and Electrical Engineering in Kyungpook National University. His research interests include electronic nose and solid electrolyte device.

Jung-Il Bang received the BS degree in engineering from Inha University in 1997. Currently, he is enrolled in master course at the School of Electronics and Electrical Engineering in Kyungpook National University. His research interests include micro-gas sensor and MEMS process.

Sang-Rok Lee received the BS degree in engineering from YeungNam University in 1998. Currently, he is enrolled in a master course at the School of Electronic and Electrical Engineering in Kyungpook National University. His research interests include tin film semiconductor type gas sensors and micro-gas sensors.

Yun-Su Lee received the BS and MS degrees in engineering from Kyungpook National University in 1995 and 1998, respectively. Currently, he is enrolled in a doctoral course at the School of Electronic and Electrical Engineering in Kyungpook National University. His research interests include electronic nose, metal oxide semiconductor type gas sensors and polymer gas sensors.

Young-Ho Song received the BS, MS and PhD degrees in engineering from Kyungpook National University in 1988, 1992 and 1996, respectively. He is currently a professor in School of Digital Electronic Engineering, Kyungwoon University, Gumi, Korea. His research interests include electronic nose, metal oxide semiconductor type gas sensors.

Duk-Dong Lee was born in Daegu, South Korea, on 21 December 1942. He received a BS degree in physics and ME degree in electronics from Kyungpook National University, Daegu, Korea, in 1966 and 1974, respectively, and a PhD degree from Yon-Sei University, Seoul, Korea, in 1984. He is currently a professor at the School of Electronic and Electrical Engineering in Kyungpook National University, Daegu, Korea. He has performed research on semiconductor gas sensors since 1978, and also performed a research in the field of humidity and optical sensors.