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Chemiresistive Sensor Array Based on Semiconducting Metal Oxides for Environmental Monitoring

Hi Gyu Moon[1,2], Soo Deok Han[1,3], Min-Gyu Kang[1], Woo-Suk Jung[1], Ho Won Jang[4], Kwang Soo Yoo[5], Hyung-Ho Park[2], and Chong Yun Kang[1,3,+]

Abstract

We present gas sensing performance based on 2×2 sensor array with four different elements (TiO_2, SnO_2, WO_3 and In_2O_3 thin films) fabricated by rf sputter. Each thin film was deposited onto the selected SiO_2/Si substrate with Pt interdigitated electrodes (IDEs) of 5 μm spacing which were fabricated on a SiO_2/Si substrate using photolithography and dry etching. For 5 ppm NO_2 and 50 ppm CO, each thin film sensor has a different response to offers the distinguishable response pattern for different gas molecules. Compared with the conventional micro-fabrication technology, 2×2 sensor array with such remarkable response pattern will be open a new foundation for monolithic integration of high-performance chemoresistive sensors with simplicity in fabrication, low cost, high reliablity, and multi-functional smart sensors for environmental monitoring.

Keywords: Gas sensors, Oxide semiconductors, TiO_2, SnO_2, WO_3, In_2O_3, Chemiresistive thin film sensor array

1. INTRODUCTION

Electronic noses based on semiconducting metal oxide sensors have been received considerable attention for many applications such as environmental monitoring system, medical fields, military systems for anti-terrorism attention for agriculture and automotive industry [1-3]. These applications are important to distinguish the specific gases in various environments [2]. In general, chemiresistive sensors based on semiconducting metal oxide thin films have a simple structure and simplicity in operation by their electrical conductivity (or resistance) which can be changed by the presence or absence of some chemical species [3,4]. In detail, the most accepted mechanism, explaining response of n-type metal oxide including TiO_2, SnO_2, WO_3, ZnO and so on, is the change of depletion layer on surface by chemisorbed oxygen at elevated temperature [4,5]. Ionized oxygen has the formation of O^{2-}, O^-, O_2^- species on the surface. Among these, O^- proved to be more reactive than O_2^-, and O^{2-}. So the response of sensor is dominated by O^-species. It was known that TiO_2 thin film gas sensors with O^- species on surface at above 250°C have a high response and fast response time to 500 ppm CO [6]. Consequently, semiconducting metal oxide gas sensors reveal the conductance change by either the adsorption and desorption of oxygen with negative charge or reaction between various gases (oxidizing gas and reducing gas) and ionized oxygen.

Semiconducting metal oxide sensors for the sensitive detection of a various gas is challenging because metal oxides have large responses to both oxidizing and reducing gases such as NO_x, CO, H_2, NH_3 and volatile organic compounds including ethanol and acetone [7]. However the semiconducting metal oxide thin film gas sensors have a low sensitivity and poor selectivity, as widely known. To solve this problem, sensor arrays based on metal oxide gas sensor with nanowire, nanobelt, and nanorod recently have been reported. Nevertheless, sensor arrays using various nanostructure have a poor stability by the change of contact region (interface) among nanostructures at high temperature and also, low reproducibility by chemical process [6,7]. As such this, the use of nanostructures is still in the beginning stage in how to

[1]Electronic Materials Research Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea
[2]Materials Science and Engineering, Yonsei University, Seoul 120-749, Republic of Korea
[3]KU-KIST Graduate School of Converging Science and Technology, Korea University, Seoul 136-701, Republic of Korea.
[4]Department of Materials Science and Engineering, Research Institute of Advanced Materials, Seoul National University, Seoul 151-744, Republic of Korea
[5]Department of Materials Science and Engineering, University of Seoul, Seoul 130-743, Republic of Korea.
[+]Corresponding author: cykang@kist.re.kr
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integrate them with low-cost and high-yield mass production process [7]. Consequently, compared with nanostructures, thin film sensors have a poor sensitivity and selectivity, but have high-yield production with low-cost and simplicity in terms of commercialization. Herein, we synthesized the chemiresistive 2×2 thin film sensor array as electronic nose composed of TiO_2, SnO_2, WO_3 and In_2O_3 thin films by rf sputter. These integrated sensor array have distinguishable pattern with high selectivity for NO_2, CO with at elevated temperature. Consequently, highly selective sensing properties of integrated 2×2 sensor array suggest the great potential for use in high performance air-quality sensors in environment.

2. EXPERIMENTAL

2.1 Fabrication of sensor array

Chemiresistive 2×2 sensor arrays which consist of four elements including TiO_2, SnO_2, WO_3, In_2O_3 were deposited onto the selected SiO2/Si substrate with Pt interdigitated electrodes (IDEs) by on-axis rf sputtering. Pt (150 nm thick) IDE patterns of 5 μm spacing were fabricated on a SiO_2/Si substrate using photolithography and dry etching. After patterning the Pt IDEs, about 100 nm thin films were deposited onto pre-specified regions (1 mm×1 mm) by a shadow mask on the Pt IDEs patterned SiO_2/Si substrate using rf sputtering at room temperature. A polycrystalline four target with 2 inch was utilized for the film deposition. At this time, the base pressure, working pressure, RF power, and gas flow rate were 2×10^{-6} mTorr, 10 mTorr, 100 W and 30 sccm, respectively. The deposition rate of the four films was about 8 nm/min. The fabricated 2×2 sensor array was annealed at 500°C for 60 min in air to crystallize thin film.

2.2 Characterization

Morphologies of the fabricated sensors array were characterized by FE-SEM (SU-70, Hitachi) using 15 kV. 2×2 sensor arrays substrate for a size comparison with a dime was photographed by digital camera (Canon EOS 650D SLR)

3. RESULTS AND DISCUSSIONS

3.1 Fabrication of sensor array

Fig. 1 shows a photo image of an integrated 2×2 sensor array,

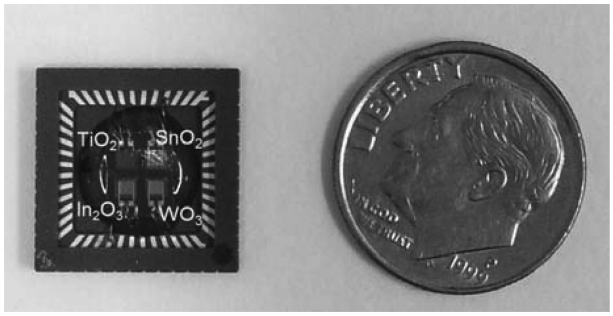

Fig. 1. Photograph of 2×2 sensor array with ceramic board for a size comparison with a dime.

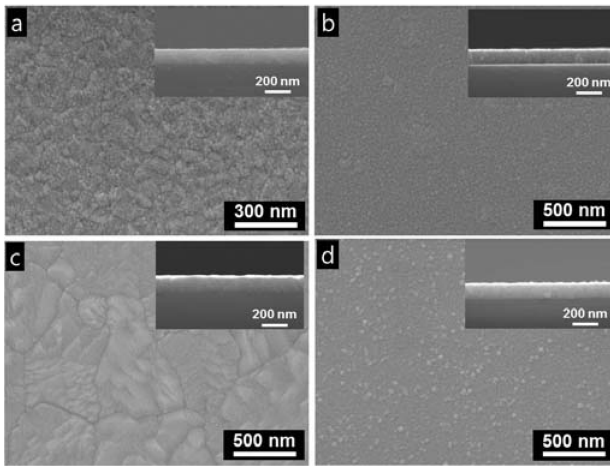

Fig. 2. A top-view and cross-sectional SEM images of (a) TiO_2, (b) SnO_2, (c) WO_3, and (d) In_2O_3 thin films deposited by rf sputter.

on top of SiO_2/Si substrate with IDE patterns of 5 μm spacing and the micro heater on the back-side of the substrate. The dimensions of the sensor array substrate are 3 mm×4 mm with the four sensing layer occupying a 1 mm×1 mm by rf sputter. In addition, this sensor array substrate does not include an integrated heater, but for sensing test attached to micro heater at the bottom of sensor in the ceramic board. Overall size of the sensor array substrate including board in the Fig. 1 has dimensions similar to that of a U.S. dime. Here, the size of the chemiresistive sensor substrate play an important rule for determining the power consumption by heating the sensor platform for gas sensing at the elevated temperature [8]. As shown in Fig. 1, these sensor arrays consist of the four different materials with TiO_2, SnO_2, WO_3, and In_2O_3, which is n-type semiconductor. Fig. 2 shows a typical top-view and cross-sectional SEM images (low magnification) of (a) TiO_2, (b) SnO_2, (c) WO_3, and (d) In_2O_3 thin films deposited by rf sputter. To make the dense thin film, each film was annealed at 500°C for 1hr in dry air and thickness is about 100 nm.

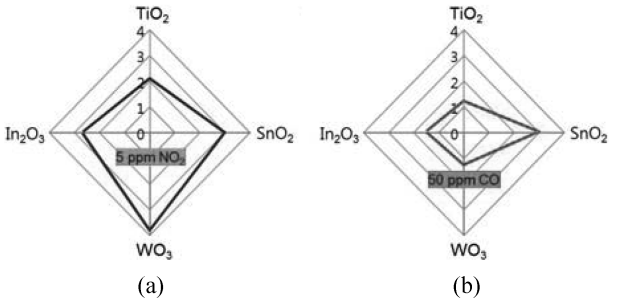

Fig. 3. Radar chart patterns of the 2×2 sensor array for (a) NO_2 5 ppm and (b) CO 50 ppm. Each vertex of the radar corresponds to each sensor of the array, where the devices were measured at 250°C with 1 V applied bias in dry air.

3.2 Sensor measurements

Fig. 3 shows radar charts of gas response toward NO_2 and CO gas species mea sured from the prototype sensor array shown in Fig. 1. For 5 ppm NO_2, the response of the WO_3 thin film gas sensor is higher than that of the TiO_2, SnO_2 In_2O_3 thin film. WO_3 itself has a high response to NO_x relative to other metal oxide semiconductors including TiO_2, SnO_2 In_2O_3, the most common material for chemoresistive sensors [7]. The sensitivity toward NO_2 gas is overall high, especially with the WO_3 sensor leading to a unique pattern, while that toward CO gas is relatively low due to low operating temperature. As shown in Fig. 3 (a) and (b), four gas sensors have its specific response pattern for different gas molecules to offer the distinguishable function of various gas species. This sensor array was used to demonstrate the feasibility as integrated e-noses. Based on the Figs. 1-3, such characteristic offers great potential to apply the fabrication methods of e-noses with excellent selectivity, high sensitivity, short response time, low power consumption, long-term stability. However, if thin film sensor arrays are exposed to high humidity (> 80%), the sensitivity of the sensor can be reduced by decreasing of the depletion area on the surface due to the change of the number of adsorbed molecules [9]. A typical response curve of the WO_3 thin film sensor to 0.5–2 ppm NO_2 at 250°C in dry air is shown in Fig. 4 (a). Upon exposure to oxidizing NO_2, the sensor quickly responds with increase in the resistance, which indicates that the WO_3 thin film is an n-type semiconductor.

As shown in Fig. 4 (b), the response curve of the SnO_2 sensor to 10–30 ppm CO at 250°C is stable gas performance with relatively fast response time and fully recovery time.

Upon exposure to oxidizing CO, the sensor responds with decrease in the resistance, which indicates the n-type semiconductor. Even at low concentration of 500 ppb, the WO_3 thin film sensor

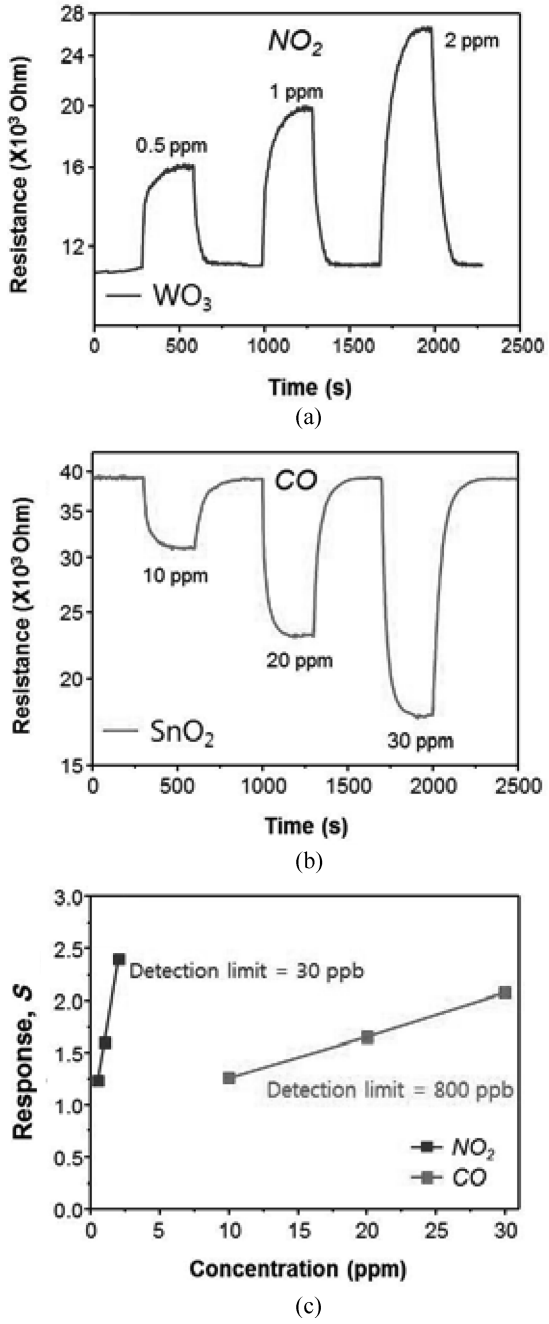

Fig. 4. (a) Dynamic sensing transients of the WO_3, (b) SnO_2 thin film sensor to 0.5–2 ppm NO_2 and 10–30 ppm Co., and (c) response of the two sensors as a function of NO_2 and CO concentration. Theoretical detection limits (DL) of sensors is presented.

shows clear response on detecting parts per billion (ppb) level NO_2 using a chemoresisitive thin film sensor in our best knowledge. In addition, for dynamic sensing transients and response to 3 consecutive pulses at NO_2 and CO concentration ranging from 0.5–2 ppm and 10–30 ppm, the resistances are fully (completely) recovered after reacting test gas. Therefore, although only two sensors are difficult to determine the performance of

sensor, it is possible for reusable sensor with very stable chemical performance. In order to estimate the NO_2 and CO detection limit of the WO_3 and SnO_2 thin film sensor, response values, S, are plotted as a function of NO_2 and CO concentration in a linear scale in Fig. 4 (c). The linear relationship between the response value and the concentration for the sensor demonstrates the feasibility and the operation capabilities of the sensor for real applications. By applying linear least-square fits to the data [10], the theoretical detection limit of the WO_3 and SnO_2 thin film sensor is estimated to be as low as 30 and 800 ppb, respectively. The CO detection limit of the sensor array is much lower than the environmental standard levels for CO (3–50 ppm) [11] .

4. CONCLUSIONS

In this work, we synthesized the chemiresistive 2×2 thin film sensor array as electronic nose composed of TiO_2, SnO_2, WO_3 and In_2O_3 thin films by rf sputter. These integrated sensor array have distinguishable pattern with high selectivity for NO_2, CO at elevated temperature. The NO_2 and CO detection limits of sensor array have as low as 30 and 800 ppb, respectively. Moreover, we expect that sensor array by rf sputter has simplicity in fabrication, low cost, higher reliability than wet process. Consequently, highly selective sensing properties of integrated 2×2 sensor array suggest the great potential for use in high performance air-quality sensors in environment.

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