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CO sensitivity of La_2O_3-doped SnO_2 thick film gas sensor

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ABSTRACT

La_2O_3-doped SnO_2 thick films were fabricated via powder mixing of SnO_2 and La_2O_3, and their sensor responses to 10–75 ppm CO were characterized. The presence of La_2O_3 in a SnO_2 thick film containing more than 1.3 at.% La_2O_3 was confirmed with X-ray diffraction performed at a slow scan rate of 0.5°/min. The sensor response to 50 ppm CO at 350 °C was improved from 9.5 to 59.0 with the addition of 2.2 at.% La_2O_3 to SnO_2. Compared to the CO sensitivity increase of the undoped SnO_2 from 3.2 to 37.6, the 2.2 at.% La_2O_3-doped SnO_2 exhibited a remarkable sensitivity improvement from 5.2 to 213.7 with an increase in the CO concentration from 10 ppm to 75 ppm.

1. Introduction

The close monitoring of polluting gases in air is crucial for health and environmental protection. The early detection of poisonous CO is particularly critical because CO is colorless and odorless and causes death by exposure to high concentrations, i.e., carbon monoxide poisoning, with symptoms such as headache, nausea, shortness of breath, dizziness and fatigue even when exposed to low concentrations [1–4].

Semiconducting metal oxides, such as SnO_2, In_2O_3, $BaTiO_3$, CuO and WO_3, have been extensively investigated for the development of low-cost resistive solid-state sensors that detect hazardous gases [1–10]. Among these metal oxides, SnO_2 may be considered the most suitable material for developing semiconductor gas sensors due to its advantages of low cost, high reliability and relatively low operating temperature [1–7]. The gas-sensing mechanism of a SnO_2 sensor in the presence of a reducing gas is based on a redox reaction at the surface. Reactions between the oxygen species chemisorbed on the SnO_2 surface with the reducing gas release electrons trapped by absorbed oxygen species into the SnO_2 matrix and result in a decrease in electrical resistivity [2,3,11,12].

Various studies have focused on the improvement of the sensing responses of SnO_2 to CO as well as CO_2 [1–7,11,12]. The incorporation of transition metal oxides such as La_2O_3, Nd_2O_3 and SrO as well as precious metals such as Pt and Pd has been known to be effective in enhancing the sensitivity of SnO_2 sensors [3,4,7,13–18]. Among transition metal oxides, La_2O_3 has been evaluated as the most appropriate additive for enhancing the CO_2 sensitivity of undoped SnO_2 from 1.1 to 1.4–1.6 [7,13,15,16]. However, the CO sensitivity of SnO_2 has been modified mostly by doping with precious metals, such as Au and Pt, and a few studies have reported the effects of La_2O_3 doping on the CO sensitivity of SnO_2 sensors [3,17,19,20]. Sensor responses of 110 and 1700 to 150 ppm and 1000 ppm CO, respectively, have been reported for Au-nanoparticle-doped SnO_2 [3].

In many previous studies on SnO_2-based sensors [2,3,5,13,14,17,18], the responses to CO have been measured at relatively high CO concentrations of 100–1000 ppm. However, the hazard of CO exposure increases dramatically at CO concentrations above 30 ppm [1]. The US Occupational Safety and Health Administration has set a general industry permissible exposure level of 50 ppm CO over an 8 h work shift, and the American Conference of Governmental Industrial Hygienists has adopted a threshold limit value of 25 ppm CO [2]. Additionally, the alarm level for CO detection is generally fixed at a CO concentration below 100 ppm. Thus, to be practically useful, the sensing characteristics of a SnO_2-based sensor must be investigated at a low concentration of CO below 100 ppm.

In this work, we characterized the responses of a La_2O_3-doped SnO_2 sensor to low concentrations of CO below 75 ppm at La_2O_3 doping contents of up to 4.3 at.%.

2. Experimental details

Commercial SnO_2 powders (99.9%), La_2O_3 powders (99.99%) of 0–4.3 mol%, and an organic binder consisting of 92 wt.% α-terpineol, 6 wt.% ethyl cellulose and 2 wt.% Triton-X were charged together in a ZrO_2 jar with ZrO_2 balls and mixed by ball-milling for 15 h to form a SnO_2 paste.

To produce an interdigitated Pt electrode, 50-nm-thick Ti and 500-nm-thick Pt layers were successively sputter-deposited on an alumina substrate and then lithographically patterned and lifted off. The 50-nm-thick Ti film was used as an adhesion layer between the Pt electrode and alumina substrate. As shown in Fig. 1, the size of the Pt electrode was 4.85 mm × 4.4 mm. The SnO_2 paste was screen-printed to a size of 5 mm × 5 mm on top of the Pt electrode on the alumina substrate and sintered at 700 °C for 2 h to form a

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La_2O_3-doped SnO_2 thick film measuring 2 μm in thickness. Because we measured the sensor characteristics of a La_2O_3-doped SnO_2 thick film in a furnace, we did not form a Pt heater on the back side of the alumina substrate.

The crystalline phases of the La_2O_3-doped SnO_2 thick films were examined by X-ray diffraction using Ni-filtered Cu Kα radiation at $2\theta = 20°–80°$ at a scan rate of 2°/min and also at $2\theta = 25°–35°$ at a slow scan rate of 0.5°/min to detect the La_2O_3 diffraction peaks. The surface morphologies of the La_2O_3-doped SnO_2 thick films were observed by field emission scanning electron microscopy (FESEM) operated at a voltage of 10 kV. The sensor responses of the La_2O_3-doped SnO_2 thick films to 10–75 ppm CO were evaluated by maintaining the sensors at 150–500 °C. The sensitivity was evaluated using the relation $S = R_{air} / R_{CO}$, where R_{air} and R_{CO} are the electrical resistances measured in air and in an atmosphere containing CO, respectively.

3. Results and discussion

Figs. 2 and 3 show the X-ray diffraction patterns of the La_2O_3-doped SnO_2 thick films sintered at 700 °C for 2 h. The Al_2O_3 peaks in Figs. 2 and 3 originated from the alumina substrate. The SnO_2 peaks in all of the samples fit the cassiterite structure, in agreement with JCPDS 77-0448. As illustrated in Fig. 2, the diffraction peaks of La_2O_3 were hardly observed in all specimens containing up to 4.3 at.% La_2O_3. For the SnO_2–LaOCl system, the diffraction peaks of LaOCl were not detected at low doping concentrations but were observed only for the 10 mol% La-doped composition [5]. However, the slow X-ray scans shown in Fig. 3 confirm the presence of La_2O_3 in the SnO_2 thick films containing more than 1.3 at.% La_2O_3. In addition to Raman scattering and XPS reported in other's work [5], slow X-ray scanning is suggested as another useful tool that can be used to detect the presence of low concentrations of La compounds in SnO_2 thick films.

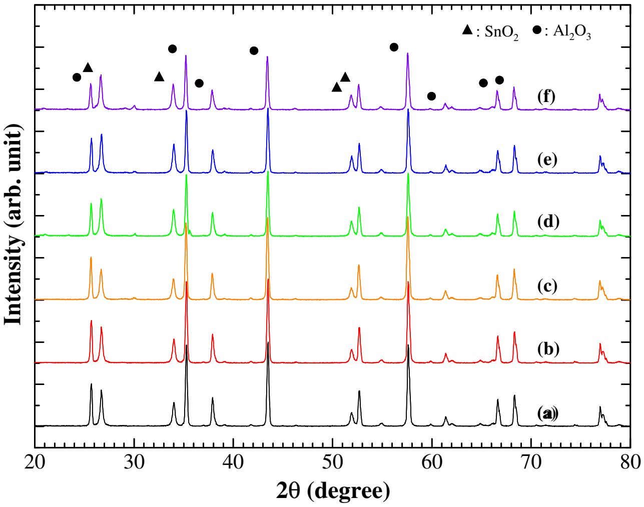

Fig. 2. X-ray diffraction patterns of the La_2O_3-doped SnO_2 thick films, measured at a scan rate of 2°/min, with a La_2O_3 concentration of (a) 0 at.%, (b) 0.4 at.%, (c) 1.3 at.%, (d) 2.2 at.%, (e) 3.3 at.%, and (f) 4.3 at.%.

Fig. 4 shows scanning electron micrographs of the undoped and La_2O_3-doped SnO_2 thick films sintered at 700 °C for 2 h. Highly agglomerated surface morphologies were observed for all specimens without appreciable differences, regardless of the La_2O_3 concentration up to 4.3 at.%, and the average particle diameter of the undoped and La_2O_3-doped SnO_2 thick films was approximately 50 nm.

The time responses of the 2.2 at.% La_2O_3-doped SnO_2 thick film to an ambient containing 50 ppm CO at different working temperatures are illustrated in Fig. 5. Considering the semiconducting nature of SnO_2, the base resistance of the 2.2 at.% La_2O_3-doped SnO_2 was expected to decrease with increasing working temperature. However, Fig. 5 shows that the base resistance in air increased from 0.04 MΩ to 1.14 MΩ with increasing working temperature from 150 °C to 500 °C. When SnO_2 is exposed to air, atmospheric oxygen is absorbed onto the SnO_2 surface, forming either molecular oxygen species O_2^- or atomic oxygen species O^- by trapping free electrons produced by ionized oxygen vacancies in SnO_2 [3,11,12]. Thus, the increase in the base resistance, shown in Fig. 5, implies that the chemisorption of more oxygen on the SnO_2 surface occurred with increasing working temperature up to 500 °C, which affected the base resistance more significantly than the semiconducting nature. Indeed, the increase in the base resistance with working temperature has been previously reported [21]. This behavior as well as the opposite, i.e., a decrease in the base resistance with working temperature, has been reported for LaOCl-doped SnO_2, depending on the LaOCl doping concentration [16].

Fig. 6 shows the CO sensitivity of the 2.2 at.% La_2O_3-doped SnO_2 thick film to 50 ppm CO at working temperatures of 150 °C–500 °C. The CO sensitivity was 1.2 at 150 °C, improved to a maximum of 59.4 at 250 °C, and then decreased with a further increase in the working

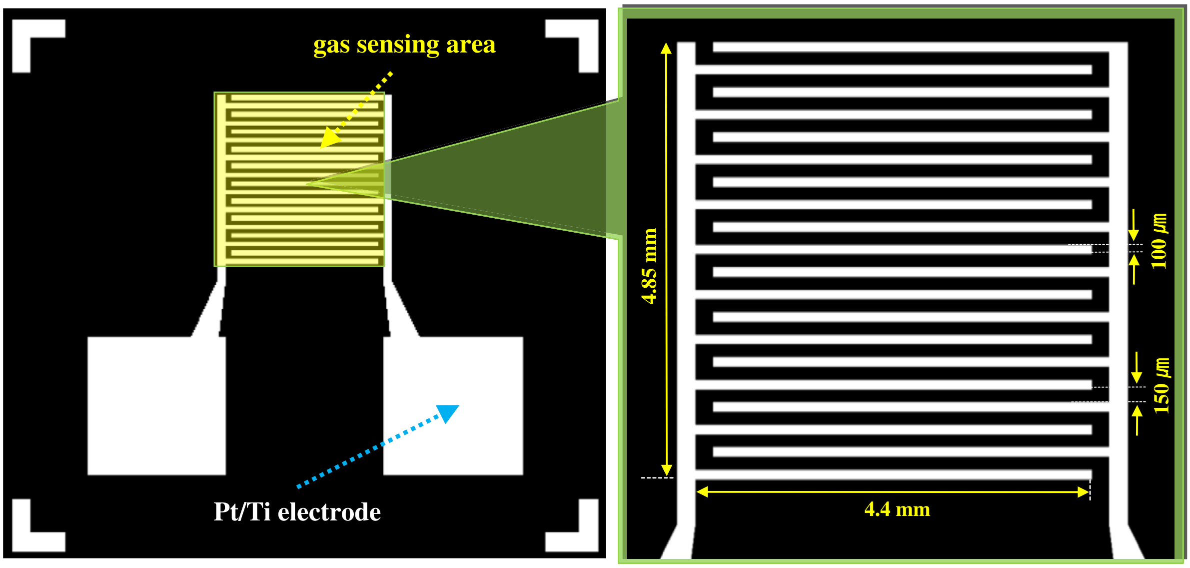

Fig. 1. Schematic illustration of an interdigitated Pt electrode.