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Carbon dioxide sensitivity of La-doped thick film tin oxide gas sensor

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Abstract

The CO_2 sensitivity of a La-doped SnO_2 thick film was characterized with variation of the La_2O_3 content up to 4.5 mol%. Effects of mechanical milling of SnO_2 powders on the CO_2 sensitivity of a SnO_2 thick film sensor were also studied. When exposed to 1000 ppm of CO_2, the sensitivity of a SnO_2 thick film sensor was improved from 1.14 to 1.52 with increasing the La_2O_3 doping concentration from 0 mol% to 2.2 mol%. Enhanced sensitivities of 1.45–1.51 were obtained for the thick film sensors processed with mechanically milled SnO_2 powders.

Keywords: A. Films; A. Milling; E. Sensors; SnO_2

1. Introduction

Gas sensors monitoring CO_2 concentrations have a wide range of applications for fire detection, indoor air quality control, biochemical process management, and agricultural and food industry [1,2]. With carbon-dioxide regulation to prevent global warming, cost-effective CO_2 sensors are highly demanded to monitor and reduce CO_2 emission [1,2]. While CO_2 sensors utilizing infrared absorption of CO_2 molecules are commonly used, they are rather bulky, expensive, and complex for maintenance [2,3]. With high reactivity of SnO_2 at a relatively low temperature, a CO_2 sensor based on SnO_2 has been extensively investigated as a candidate to replace an optical detection system [3–6].

Various works have been performed to improve CO_2 sensing characteristics of a SnO_2 thick film sensor. Doping of transition metal oxides such as lanthanum oxide, niobium oxide, antimony oxide, and strontium oxide as well as incorporation of precious metals such as Pt has been known to be an effective method to promote a sensitivity of a SnO_2 thick film sensor [3–6]. Among transition metal oxides, lanthanum oxide has been reported to be the most appropriate additive to improve CO_2 sensitivities of not only a SnO_2 thick film sensor, but also a $BaTiO_3$ thick film device [6,7]. Various works have been conducted with coating, impregnation, and powder-mixing to process La-doped SnO_2 sensors. While most of works have involved in incorporation of LaOCl as a lanthanum oxide additive, however, there were not many reports for the SnO_2 thick film sensors processed by powder mixing of SnO_2 and La_2O_3 [3–6].

The gas detection principle of a solid state CO_2 sensor is based on conductivity change caused by chemisorptions and gas–solid reactions at the sensor surface [2,8]. The sensitivity of a CO_2 sensor is dependent upon the surface area of a thick film sensor which can be increased by utilizing powders of a reduced size or highly agglomerated powders to get poor sinterability [9]. With repeated fracture and cold welding during the process, mechanically milled powers become highly refined and agglomerated, resulting in poor sinterability [10]. Thus, mechanical milling of SnO_2 powders can be a good method to increase the surface area of a thick film sensor by reducing a powder size and facilitating agglomeration of powders.

In this work, we investigated the CO_2 sensitivity of a La-doped SnO_2 thick film with variation of the La_2O_3 content up to 4.5 mol%. We also studied effects of mechanical milling of SnO_2 powders on the CO_2 sensitivity of a SnO_2 thick film sensor.

2. Experimental

Commercial SnO_2 powders (99.9%) and La_2O_3 powers (99.99%) of 0–4.5 mol% were mixed with organic binder by ball-milling for 15 h to form SnO_2 paste. To make Pt electrodes of interdigit configuration, a 50 nm-thick Ti and a 500 nm-thick

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Pt were successively sputter-deposited on an alumina substrate and then lithographically patterned by lift-off method. The 50 nm-thick Ti was used as an adhesion layer between Pt electrodes and an alumina substrate. SnO_2 paste was screen-printed to a size of 5 mm × 5 mm on an alumina substrate and fired at 700 °C for 2 h. Thickness of a SnO_2 thick film was controlled to be about 2 μm. As we measured sensor characteristics in a furnace, we did not form a Pt heater on the back side of an alumina substrate.

For mechanical milling, SnO_2 powders were charged under Ar atmosphere in a hardened tool steel vial with steel balls as milling media. The ball-to-material weight ratio was held at 10:1. Mechanical milling was conducted by shaking a vial at approximately 1200 rpm using a Spex mixer/mill (SPEX SamplePre-8000 M, USA) for 10–30 min. Mechanically milled SnO_2 powders were mixed with organic binder by ball-milling for 15 h, screen printed on an alumina substrate with Pt electrodes, and fired at 700 °C for 2 h to form a SnO_2 thick film.

X-ray diffraction analysis (RIGAKU ULTIMA IV, Japan) was performed for La_2O_3-doped SnO_2 thick films. Surface morphologies of the thick films and the mechanically milled powders were observed with scanning electron microscopy (HITACHI S-4300, Japan). A sensor response to 1000 ppm CO_2 was evaluated by maintaining a sensor at 350–500 °C in a furnace. Gases were fed to the quartz tube in a furnace using mass flow controllers. Resistances between Pt electrodes were measured with a semiconductor characterization system (KEITHLEY 4200-SCS, USA) in air and in an ambient containing 1000 ppm CO_2. A sensitivity, S, was evaluated by using the relation of $S = R_{air}/R_{CO_2}$, where R_{air} and R_{CO_2} are the electrical resistances measured in air and in the ambient containing 1000 ppm CO_2, respectively.

3. Results and discussion

Fig. 1 represents the response characteristics of an undoped-SnO_2 thick film exposed to 1000 ppm CO_2 at different working temperatures. Resistance of an undoped-SnO_2 sensor in air decreased with increasing a working temperature because of semiconducting nature of SnO_2. Response to CO_2 exposure also decreased with increasing a working temperature due to less absorption of CO_2 to the sensor surface at higher temperature [11]. Resistance decrease with CO_2 exposure, shown in Fig. 1, implied that CO_2 behaved as a reducing gas in our experiment. Reactions between CO_2 and oxygen species chemisorbed on the SnO_2 surface prior to CO_2 exposure release electrons trapped by the absorbed oxygen species into SnO_2 matrix, resulting in a resistance decrease [4]. However, it is controversial whether CO_2 works as a reducing or an oxidizing gas to SnO_2. Although many literatures supported our results, there were also other reports revealing a resistance increase with CO_2 exposure [3–6]. As shown in Fig. 2, the CO_2 sensitivity of an undoped-SnO_2 thick film decreased from 1.16 to 1.11 with increasing a working temperature from 350 °C to 500 °C probably due to less chemisorptions of CO_2 on the sensor surface [11]. On the other hand, a response to CO_2 exposure could not be detected at a temperature below 350 °C.

Fig. 3 represents X-ray diffraction patterns of La_2O_3-doped SnO_2 thick films. Alumina peaks in Fig. 3 were originated from an alumina substrate. No differences were detected in the X-ray diffraction patterns of the SnO_2 thick films undoped or doped with La_2O_3 up to 4.5 mol%. For SnO_2–LaOCl system, it has been also reported that diffraction peaks of LaOCl were not detected for compositions of low dopant concentrations, but observed only for the 10 mol% La-doped composition [4].

Fig. 4 illustrates the CO_2 sensitivities of La_2O_3-doped SnO_2 thick films measured at 400 °C. The sensitivity increased from 1.14 to 1.52 with increasing the La_2O_3 concentration up to 2.2 mol% and then decreased with further increasing the amount of La_2O_3 additives. Such bell-shaped behavior of the sensitivity improvement with the La concentration was also reported by others [6]. As a sensitivity improvement mechanism of the La-doped SnO_2, Kim et al. suggested sensing reaction enhancement at the interface between SnO_2 and lanthanum oxide [6]. On the other hand, Yoshioka et al.

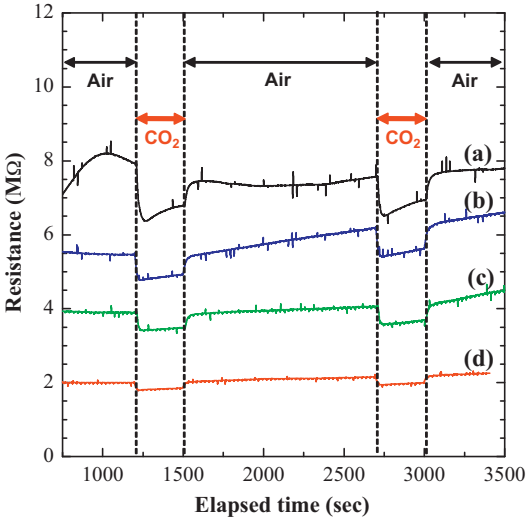

Fig. 1. CO_2 responses of an undoped SnO_2 thick film at a working temperature of (a) 350 °C, (b) 400 °C, (c) 450 °C, and (d) 500 °C.

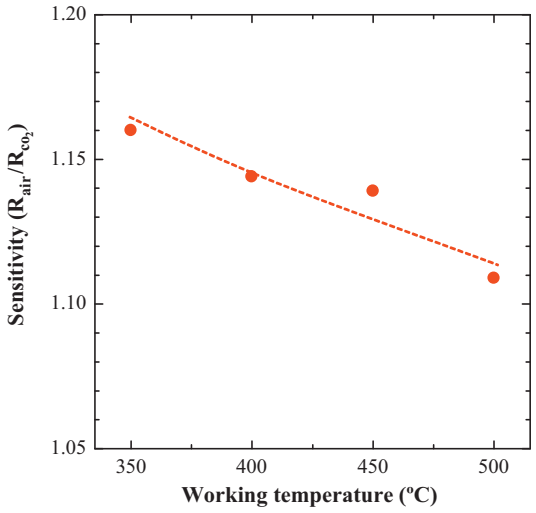

Fig. 2. CO_2 sensitivity of an undoped SnO_2 thick film as a function of the working temperature.

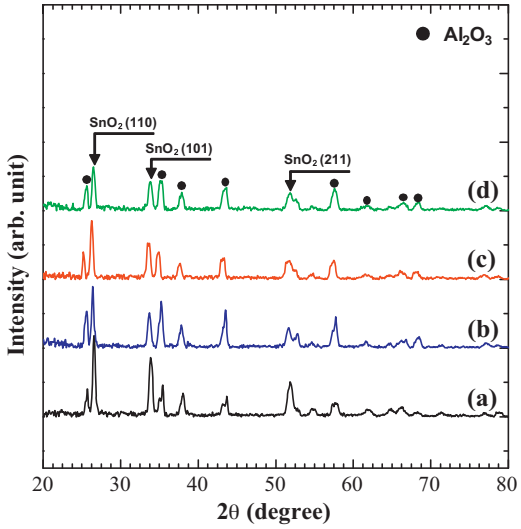

Fig. 3. X-ray diffraction patterns of the SnO_2 thick films doped with La_2O_3 of (a) 0 mol%, (b) 1.3 mol%, (c) 2.2 mol%, and (d) 4.5 mol%.

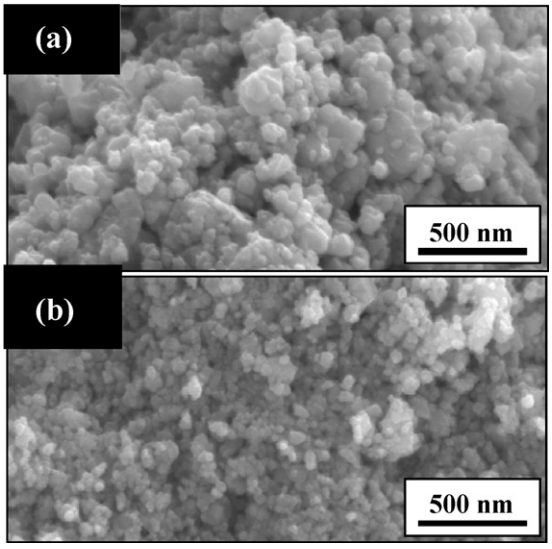

Fig. 5. SEM micrographs of the SnO_2 powders (a) before and (b) after mechanical milling for 30 min.

proposed that the La-doped SnO_2 surface facilitated absorption of CO_2 [5,12]. However, detailed mechanisms for sensitivity improvement in La-doped SnO_2 have not been fully understood yet. The sensitivity decreased from 1.52 to 1.17 with increasing the La_2O_3 concentration from 2.2 mol% to 4.5 mol%.

In Fig. 5, the morphology of the SnO_2 powders mechanically milled for 30 min was compared with that of the powders without mechanical milling treatment. SnO_2 powders were refined by mechanical milling treatment for 30 min, implying that mechanical milling was an effective method to reduce a particle size of ceramic powders in a short time. Fig. 6 represents the sensitivity of the SnO_2 thick films measured at 500 °C as a function of mechanical milling time up to 30 min. The sensitivity was improved from 1.11 to 1.45–1.51 for the sensors processed with mechanically milled SnO_2 powders, which could be partly due to a reduced particle size of the

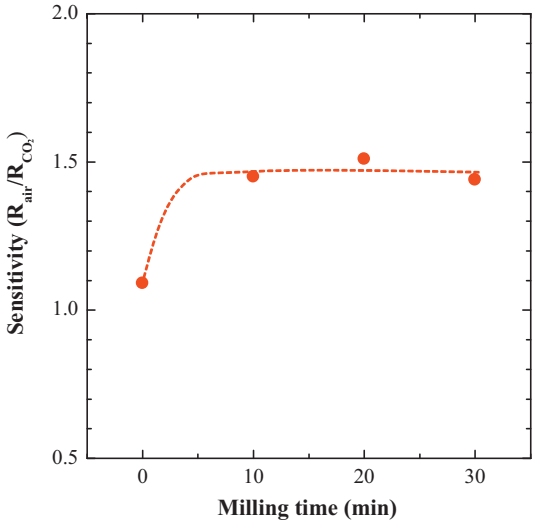

Fig. 6. CO_2 sensitivity of the SnO_2 thick films as a function of the mechanical milling time.

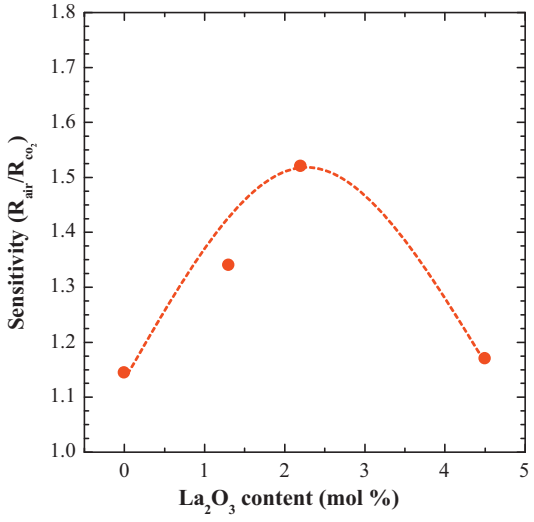

Fig. 4. CO_2 sensitivity of the SnO_2 thick films as a function of the La_2O_3 concentration.

mechanically milled powders as shown in Fig. 5. Variation of the sensitivity with the mechanical milling time above 10 min was not noticeable, implying that the sensitivity would be improved abruptly by mechanical milling longer than a threshold milling time. Although further works are required to understand the details of mechanical milling effects, the results in Fig. 6 confirm that mechanical milling treatment of SnO_2 powders is an effective method for the sensitivity improvement of a SnO_2 thick film sensor.

4. Conclusion

With increasing a working temperature from 350 °C to 500 °C, the sensitivity of an undoped-SnO_2 thick film to 1000 ppm CO_2 decreased from 1.16 to 1.11 due to less chemisorptions of CO_2 on the sensor surface. The CO_2

sensitivity at 400 °C increased from 1.14 to 1.52 with increasing the La_2O_3 doping concentration up to 2.2 mol%, and then decreased with further increasing the amount of La_2O_3 additive. Average particle size of SnO_2 powders was reduced by mechanical milling treatment for 30 min, implying that mechanical milling was an effective method to reduce a particle size of ceramic powders in a short time. The CO_2 sensitivity was improved from 1.11 to 1.45–1.51 by mechanical milling treatment of SnO_2 powders partly due to a reduced particle size of mechanically milled powders. Mechanical milling treatment of SnO_2 powders could be thought as an effective method for the sensitivity improvement of a SnO_2 thick film sensor.

Acknowledgement

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