CO_2 Sensing Properties of La-loaded SnO_2 Thin Films Prepared by Sputtering

Hiroshi Sakama, Shinji Saeki, Atsushi Ono, Noriya Ichikawa, Atsushi Tanokura, Hiroshi Uetsuka,[†] and Hiroshi Onishi[†]
Department of Physics, Sophia University, 7-1, Kioi-cho, Chiyoda-ku, Tokyo 102-8554
[†]Surface Chemistry Laboratory, Kanagawa Academy of Science and Technology,
KSP East 404, 3-2-1 Sakado, Takatsu-ku, Kawasaki Kanagawa 213-0012

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The detection sensitivities of La-loaded SnO_2 films prepared using reactive RF magnetron sputtering to CO_2 were measured at various temperatures. The maximum sensitivity was attained at 200 °C for a film loaded with 5 atom % La. Pure SnO_2 films revealed good crystallinity of the rutile phase. The crystallization of SnO_2 films was suppressed by La loading.

Exact measurement of the carbon dioxide (CO_2) concentration in air is important for the ventilation of houses and buildings. In addition, it is important for the precise control of industrial processes such as fermentation, cultivation, and the combustion of fuel.

Semiconductor gas sensors have been widely used to detect combustible gases.[1] The concentrations of gases in air are evaluated by means of resistance changes with and without gas adsorption on sensor surfaces. However, semiconductor sensors are not believed to be effective for sensing CO_2 because sensor resistances hardly change with the adsorption of CO_2 molecules. Therefore, a nondispersive infrared analyzer (NDIR) and solid electrolytes are generally utilized to sense CO_2.[2,3]

Iwamoto and co-workers first reported an improvement in the sensing properties of CO_2 using SnO_2 sensor by metal oxide loading.[4,5] Among the metal oxides, they demonstrated that La_2O_3-loaded sensors have superior properties (maximum sensitivity and shortest response time) compared with other metal oxide loaded sensors. Sensor elements were composed of thick SnO_2 films deposited on alumina substrates. SnO_2 films were impregnated with Lanthanum nitrate and calcined at a high temperature to form La_2O_3-loaded sensors.

In general, sensor elements are composed of sintered semiconductor materials. However, a common problem in thus prepared sensors is the fluctuation in sensing properties among sensors because of the variation in grain size and oxidative state of semiconductors. Semiconductor gas sensors have also been successfully fabricated using thin-film fabrication processes including the sol–gel method, sputtering, and chemical vapor deposition from the view point of reproducibility in sensing properties.[6–8] Among the techniques available for fabrication of SnO_2 thin films, sputtering is advantageous in its production of films with high mechanical durability, low growth temperatures and easy process control. However, no attempts have yet been made to detect CO_2 using SnO_2 sensors prepared by sputtering.

The aim of this study was to produce La_2O_3-loaded SnO_2 films by sputtering and to evaluate the CO_2 sensing properties of the films.

SnO_2 thin films were prepared using reactive RF magnetron sputtering. A 100-mm diameter tin disc with 4N purity was used as a target. Slide glasses ($20 \times 20 \times 1$ mm; Length×width×thickness) were used as substrates. The ambient atmosphere during sputtering was composed of a mixture of Ar and O_2. The best crystallinity of pure SnO_2 films was obtained at flow rates for Ar and O_2 of 50 sccm and 15 sccm, respectively. Sputtering was performed at room temperature. The total gas pressure, sputtering power and sputtering time were fixed at 6.0×10^{-3} Torr, 200 W and 2 h, respectively. The sample-target distance was 30 mm. The thickness of the films was approximately 400 nm. Loading of La into the films was achieved by cosputtering La_2O_3 powder placed on the target. The concentration of La in the films was controlled by changing the weight of the powder. No post-annealing of sputtered films was conducted.

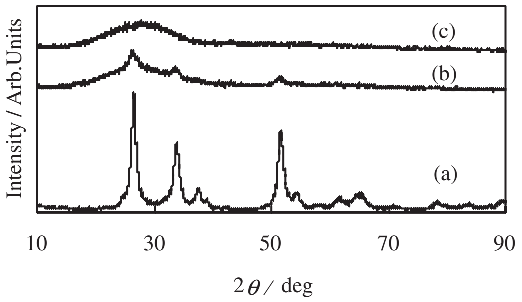

Figure 1. XRD patterns for SnO_2 films: (a) pure SnO_2, (b) La 2 atom %, (c) La 5 atom %.

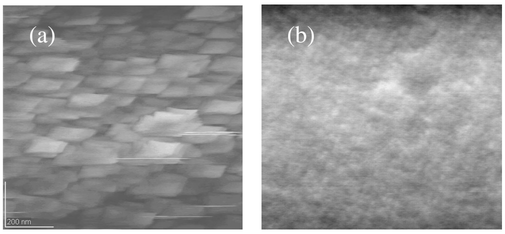

Figure 2. AFM images for SnO_2 films: (a) pure SnO_2, (b) La 5 atom %. Image sizes are 1×1 μm.

The resistance of the film was measured using the two-point probe method. Measurements were carried out at room temperature and at the elevated temperatures. The two electrodes consisted of Au films. The current was strictly proportional to the applied voltage in the range from 0 to 50 V. The resistance was established by the slope of the plot of the current vs the voltage. The detection sensitivity of the film to CO_2 was defined as the ratio of the film resistance in air (R_{air}) to that at certain CO_2 concentration (R_{gas}).

Figure 1 shows the XRD patterns for SnO_2 films loaded with and without La. The pattern from the pure SnO_2 film revealed sharp diffraction peaks with little background, indicating good

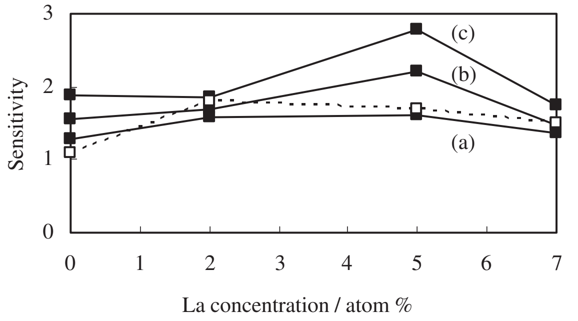

Figure 3. The sensitivity to CO_2 as a function of La concentration measured at room temperature (solid lines). CO_2 concentrations are (a) 100 ppm, (b) 0.1%, and (c) 1%, respectively. Dashed line denotes the sensitivity reported in Ref. 9.

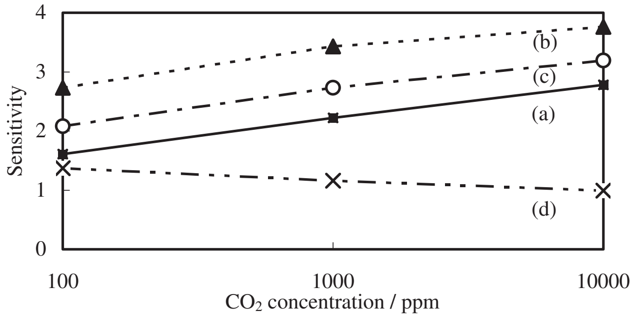

Figure 4. The sensitivity as a function of CO_2 concentration measured at various temperatures for a film loaded with 5 atom % La. The detection temperatures are (a) room temperature, (b) 200 °C, (c) 400 °C, and (d) 500 °C, respectively.

crystallinity of the rutile phase. The background intensity increased and the intensities of peaks dropped as the concentration of La in the films increased. In particular, films with more than 2 atom % La show no sharp peaks. This observation indicates that crystallization of SnO_2 films was suppressed by La loading.

Figure 2 shows AFM images for SnO_2 films. Rectangle-like grains with the size of approximately 100 nm were observed in the pure SnO_2 film, whereas grains in the film loaded with 5 atom % La were much smaller (10 nm). The AFM images are in good agreement with the XRD patterns.

The XPS spectra for La 3d states of the films revealed that La is fully ionized (La^{+3}) in the films in an oxidative atmosphere of sputtering gas.

The dependence of the detection sensitivity to CO_2 on the La concentration measured at room temperature is shown in Figure 3. The sensitivity increased with La concentrations less than 5 atom %, whereas it decreased with further La loading. The maximum sensitivity was achieved at 5 atom % La, irrespective of the CO_2 concentration. The sensitivity obtained in a 1% CO_2 atmosphere is 2.78. The optimum concentration of La (5 atom %) is larger than that reported in the literature (1.5 atom %).[4] It was demonstrated that sensor elements prepared by calcination contain a considerable amount of impurities and La exists in the form of hydroxide. The sensing properties degenerate over several days in air owing to humidity.[9] In degenerated sensors, La aggregated in large precipitates ($La_2O(CO_3)_2 \cdot xH_2O$). Additional additives (Y, Gd, Mg) were necessary to maintain the stability of the sensor properties by preventing the aggregation of La. Excessively loaded La (more than 1.5 atom %) was thought to be inactive in the presence of water vapor.[10] In contrast, there is no need to add other additives to our films, as the sensitivities were determined to be stable for at least one month. Therefore, more La atoms (up to 5 atom %) are active and free from deactivation by water vapor in our films. This is possibly due to the high purity of the sputtered films because XPS spectra showed no trace of impurity in films.

Alternatively, the optimum concentration of La may be closely related to the morphology of the films. The sensitivity of SnO_2 sensors to hydrogen was shown to be greatly increased with the grain size less than 6 nm, which is comparable to the size shown in Figure 2b.[11] Similar size effect may play an important role in enhancement of sensitivity by La loading.

The influence of the detection temperature upon sensitivity is shown in Figure 4 for a film loaded with 5 atom % La. The sensitivity monotonically increased with the logarithm of CO_2 concentration at all temperatures with the exception of 500 °C. It also increased with the detection temperature up to 200 °C, while decreased with further rising of the detection temperature. Thus, the maximum sensitivity was obtained at 200 °C. The sensitivity in a 1% CO_2 atmosphere (3.76) at 200 °C is much higher than that reported for the sensor prepared by calcination (1.79 measured at 2080 ppm CO_2, 400 °C).[4] This phenomenon may be due to a larger concentration of La in the films available for CO_2 detection.

In conclusion, La-loaded SnO_2 films were prepared using reactive RF magnetron sputtering, and the detection sensitivities to CO_2 were measured at various temperatures. The maximum sensitivity of 3.76 at 1% CO_2 was attained at 200 °C for a film loaded with 5 atom % La. Pure SnO_2 films revealed good crystallinity of the rutile phase, whereas the crystallization of SnO_2 films was suppressed upon La loading.

References and Notes

1 T. Seiyama, A. Kato, K. Fujishima, and N. Nagatani, *Anal. Chem.*, **34**, 1502 (1962); T. Hirabayashi, *Sens. Technol.*, **6**, 78 (1986).
2 P. J. Medvecz and K. M. Nichols, *Appl. Spectrosc.*, **46**, 1887 (1992).
3 T. Ogata, S. Fujitsu, M. Miyayama, K. Koumoto, and H. Yamagida, *J. Mater. Sci. Lett.*, **5**, 285 (1986).
4 T. Yoshioka, N. Mizuno, and M. Iwamoto, *Chem. Lett.*, **1991**, 1249.
5 N. Mizuno, T. Yoshioka, K. Kato, and M. Iwamoto, *Chem. Lett.*, **1992**, 2467.
6 C. Garzella, E. Comini, E. Tempesti, C. Frigeri, and G. Sberveglieri, *Sens. Actuators, B*, **68**, 189 (2000).
7 V. Guidi, D. Boscarino, E. Comini, G. Faglia, M. Ferroni, C. Malagu, G. Martinelli, V. Rigato, and G. Sberveglieri, *Sens. Actuators, B*, **65**, 264 (2000).
8 H. Kim and C. G. Park, *J. Electrochem. Soc.*, **138**, 2408 (1991).
9 M. Hanada, H. Koda, K. Onaga, and T. Onouchi, Proc. 7th Sensor 95, (1995), p 445.
10 M. Hanada, K. Onaga, M. Nishiguchi, and T. Onouchi, *Chem. Sens.*, **15B**, 130 (1999).
11 H. Ogawa, M. Nishikawa, and A. Abe, *J. Appl. Phys.*, **53**, 4448 (1982).