

## Long-term stabilized metal oxide-doped SnO<sub>2</sub> sensors

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### Abstract

TiO<sub>2</sub>, ZrO<sub>2</sub>, and SiO<sub>2</sub> were added in the concentration of 1-3 wt.% to improve long-term stability for the SnO<sub>2</sub> thick film gas sensor. Short-term sensor resistances up to 90 h were measured to investigate the stabilization time of initial resistance in air. Long-term resistance drifts in air and in gas to 5000 ppm methane for the sensors annealed at 750 °C for 1 h and continuously heated at an operating temperature of 400 °C were also measured up to 90 days at an interval of 1 day. The long-term drifts in methane sensitivity for the three metal oxide-doped SnO<sub>2</sub> sensors are closely related to methane sensitivity level, catalytic activity, and long-term drift in sensor resistance in air. Those stabilities are mainly discussed in terms of oxidation state and catalytic activity.

**Key Words** : thick film sensor, long-term stability, catalytic activity; drift in resistance

### 1. Introduction

There is a great demand for monitoring a hydrocarbon gas for the purpose of control and safety applications in domestic and industrial fields. SnO<sub>2</sub> semiconductor gas sensors are now widely used to detect hydrocarbon gases. Gas sensing devices are required to have such general properties as high sensitivity, fast response, moderate selectivity, long lifetimes, and low power consumption<sup>[1-3]</sup>. SnO<sub>2</sub> sensors are considered as the best material to meet all these requirements. However, the main disadvantage includes continuous electric power for the sensor heating that causes long-term sensitivity drift. Some units have been often operated continuously for over ten years. Many problems arising from the long-term operation are sensitivity drift, humidity influence and wide variation in sensor resistance. Unfortunately, these problems are directly related to the reliability of the gas sensor. Such long-term change in sensitivity that causes false alarm or monitoring indication, requires customer periodic recalibration for a critical application<sup>[4,5]</sup>.

Long-term stability might be closely dependent on stabilizing SnO<sub>2</sub> crystallite growth, oxidation reactivity of a test gas, micro-structural change, polymerization of a binder when using organic binder, densification of SnO<sub>2</sub> during sintering, and physical and chemical reactions with contaminated atmosphere such as high humidity conditions or existence of a reactive gas, and other complicated factors<sup>[6]</sup>. Adding a certain kind of dopant to SnO<sub>2</sub> as so-called crystallite growth inhibitors seems to be very effective to improve long-term stability. SnO<sub>2</sub> crystallite could be stabilized by adding B, Ba, Sm, P, Mo, W, Ca, Sr, Cr and In<sup>[7-9]</sup>. Long-term stabilizing effect of such additives may be significant for a SnO<sub>2</sub> sensor sintered at lower temperatures and operated at higher temperatures. Nakamura *et al.*<sup>[10]</sup> and Matsuura *et al.*<sup>[11-13]</sup> have reported that the long-term drift of the sintered SnO<sub>2</sub> sensors results from various causes such as decrease in catalytic activity, change in resistance by surface hydroxyl group, and rise in sensor's temperature due to heat of combustion of the target gas. The surface hydroxyl groups directly affect the sensor resistance as well as the catalytic activity of the sensor element. In order to improve long-term stability of the SnO<sub>2</sub> sensor, both reversible (surface reaction due to presence of water vapor) and irreversible (decrease in catalytic activity caused by a decrease in the number of hydroxyl groups on the oxide surface) changes must be controlled. It has been suggested<sup>[11]</sup> that the long-term stability of sintered SnO<sub>2</sub> gas sensors is greatly

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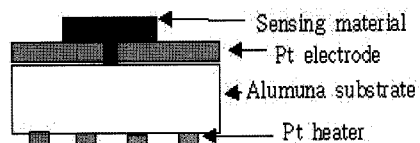
improved by addition of rhenium and vanadium. Most commercially available hydrocarbon sensors are in a sintered  $\text{SnO}_2$ -based type. Amorphous thin film type gas sensors are formed by physical vapor deposition followed by annealing. The amorphous films experience phase transformation and change in surface area during the heat treatment. Oxide films sputtered under a low oxygen vapor pressure include metallic constituents of low valence. In this case, long-term stability is mainly affected by structural density and phase stability of the oxide film<sup>[14,15]</sup>. Significant change in microstructure and density of a  $\text{SnO}_2$  thin film sensor may be undergone at a high operating temperature, especially when it has more than two structural phases containing some metastable or unstable phases and fine particles in a sintered state.

Few studies have been carried out on long-term methane sensitivity change of the thick film ceramic sensor. In this study, various metal oxides were added to investigate long-term stability for the  $\text{SnO}_2$  sensors at a fixed relative humidity (RH).  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{SiO}_2$  were selected in order to prevent the progress of sintering of the crystalline materials<sup>[16]</sup> because all these n-semiconducting oxides may inhibit crystal growth at a working temperature in use. To simplify the effect of the additives on long-term stability, noble metal catalysts were not doped in the  $\text{SnO}_2$  thick films and the oxides as additives were selected because of the same metallic valency as  $\text{SnO}_2$ . Methane among various hydrocarbon gases was chosen as the test gas because  $\text{SnO}_2$  sensors exhibited very low sensitivity to chemically stable gases such as methane. Doping effects on short-term and long-term sensor resistances were also investigated and discussed.

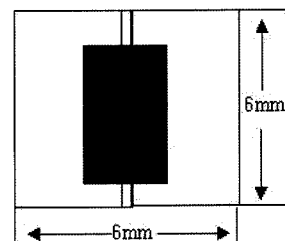
## 2. Experimental

The preparation method of sensor elements and sensitivity measurements have been described elsewhere<sup>[9]</sup>.  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , and  $\text{SiO}_2$  (MO) powders were added in concentration of 1-3 wt.% (in weight percent) to  $\text{SnO}_2$  powder previously prepared at pH 11.3 in 0.12 M of stannous chloride solution by wet chemical method.  $\text{SnO}_2$  powders mixed with those metal oxides were dried at 110 °C for 26 h and calcined at 600 °C for 2 h with subsequent milling in the ball mill containing  $\text{Si}_3\text{N}_4$  balls of 5 mm diameter for 24 h. A pair of 3000 Å

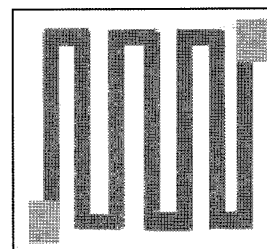
thick Pt electrodes was ion-coated on an alumina sheet. The MO-doped  $\text{SnO}_2$  pastes were screen-printed on alumina with the Pt electrodes. 15 wt.% ethylene glycol was used as a binder in the  $\text{SnO}_2$  gas sensor in order to enhance the sintering strength. As a preliminary test, when distilled water as a binder was attempted, the fabricated sensor exhibited poor  $\text{CH}_4$  sensitivity. The 40  $\mu\text{m}$  thick-film device was sintered at 700 °C, 750 °C and 800 °C for 1 h. Short-term and long-term sensor resistances, and the  $\text{CH}_4$  sensing characteristics were measured at an operating temperature of 400 °C in a heated chamber of 10 liter. Before the sensitivity measurements, the sensors were stabilized in the same chamber at the operating temperature for 4 days. Throughout this study, long-term sensitivity measurements were carried out up to 90 days for 5000 ppm  $\text{CH}_4$  at 30 % of relative humidity in ambient. Relative humidity was measured at 25 °C by using THERMO-HYGROME-



(a) cross section



(b) front side



(c) back side

Fig. 1. Schematic diagrams of sensor structure.

TER (Sato Keiryoki Mfg. Co.) that indicates ambient temperature and relative humidity. Our sensor structure is illustrated in Fig. 1.

The sensitivity (*S*) is expressed in terms of sensor resistance in air, *R<sub>a</sub>*, and in the test gas, *R<sub>g</sub>*, as follows:

$$S = R_a / R_g \quad (1)$$

### 3. Results and discussion

As an undoped SnO<sub>2</sub> sensor exhibits a limited sensitivity to chemically stable gases such as methane, high sensitivity to methane is first aimed to obtain the optimal experimental condition for the long-term stability test. A plot of gas sensitivity to 5000 ppm methane vs. percentage of MO as dopant is given in Fig. 2.

The MO-doped SnO<sub>2</sub> samples were sintered at 750 °C for 1 h. The undoped SnO<sub>2</sub> sensor element exhibits 2.8 of methane sensitivity at the operating temperature of 400 °C. 2-3 wt. % additions of all the three oxides to SnO<sub>2</sub> result in sensitivity enhancement compared to the undoped sensor element. TiO<sub>2</sub>-doped sensors have significantly high methane sensitivity in spite of the sensors having no noble metal catalyst. It is found that the addition of all these oxides up to 3 wt.% improves methane sensitivity. According to C. Xu *et al.* [17], gas sensitivity of SnO<sub>2</sub> element is strongly dependent on the crystallite size of SnO<sub>2</sub> included, decreasing with increasing crystallite size. Respective crystallite sizes of SnO<sub>2</sub> doped in concentrations of 1 wt.% and 3 wt.% are 290 Å and 261 Å for TiO<sub>2</sub>, 281 Å and 254 Å for ZrO<sub>2</sub>, and 270 Å and 249 Å for SiO<sub>2</sub>. Thus, improvement of

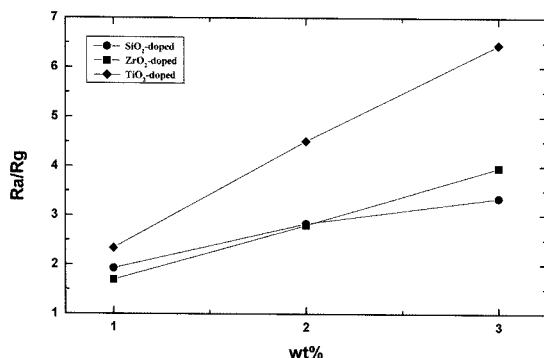


Fig. 2. Sensitivity to 5000 ppm CH<sub>4</sub> as a function of MO content in SnO<sub>2</sub> thick film sensors sintered at 750 °C for 1 h.

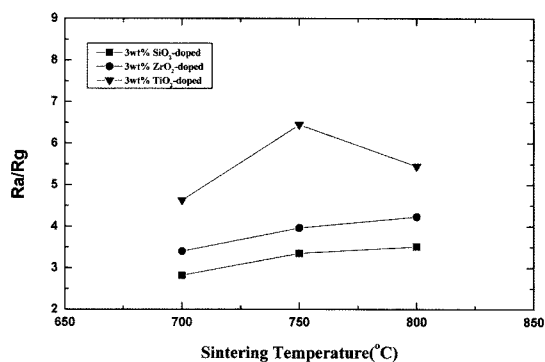


Fig. 3. Sensitivity to 5000 ppm CH<sub>4</sub> as a function of sintering temperature in 3 wt.% MO-doped SnO<sub>2</sub> thick film sensors sintered at 750 °C for 1 h.

methane sensitivity may arise from the decrease of crystallite size by adding such oxides. TiO<sub>2</sub> doped- SnO<sub>2</sub> sensors exhibited the highest methane sensitivity, resulting from the catalytic activity of TiO<sub>2</sub> as consistent with Lee's results [18].

Variation of 5000 ppm methane sensitivity with sintering temperature for 3 wt.% MO-doped SnO<sub>2</sub> sensors is shown in Fig. 3. Sintering of 3 wt.% TiO<sub>2</sub>-doped SnO<sub>2</sub> sensors at 750 °C gives the highest sensitivities as well as enough mechanical strength of the thick film. Hereafter, 3 wt.% MO-doped SnO<sub>2</sub> sensors sintered at 750 °C for 1 h are mainly considered.

Phases included are identified by using X-ray diffractometer (XRD: Rigaku D-MAX 2500). XRD patterns for 3 wt.% MO-doped SnO<sub>2</sub> powders are shown in Fig. 4. 3 wt.% is within the solubility limit for SiO<sub>2</sub> and ZrO<sub>2</sub>

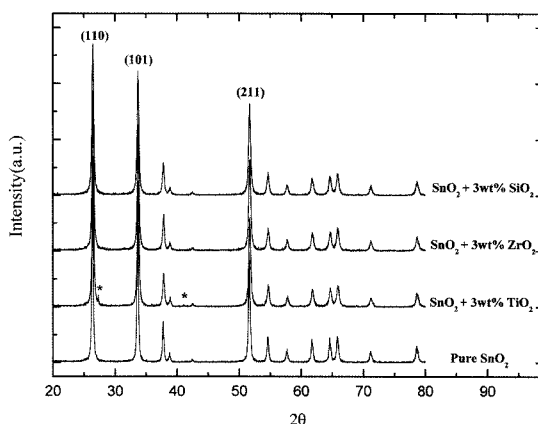


Fig. 4. XRD spectra of 3 wt.% MO-doped SnO<sub>2</sub> powders sintered at 750 °C for 1 h.

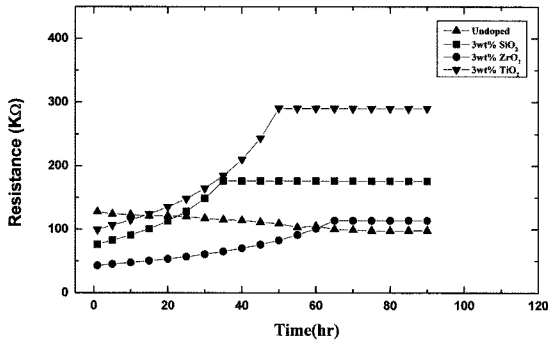
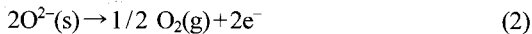


Fig. 5. Short-term resistance transient of MO-doped SnO<sub>2</sub> sensors at an operating temperature of 400 °C.

dopants. However, solubility of TiO<sub>2</sub> in SnO<sub>2</sub> is less than 3 wt.%, as expected from the appearance of pure TiO<sub>2</sub> phase.

Short-term sensor resistances were measured at the operating temperature of 400 °C up to 90 h. As shown in Fig. 5, the resistance of the undoped SnO<sub>2</sub> sensor decreases slightly while resistances of the MO-doped SnO<sub>2</sub> sensors increase.

According to Matsuura *et al.*<sup>[12]</sup>, time-dependent resistance in air,  $R_a$ , of energized undoped SnO<sub>2</sub> sensor at 350 °C hardly changed, while that of the sensors at 450 °C decreased. It has been suggested that the decrease in  $R_a$  for the energized sensors at 450 °C without binder might be caused by free electrons generated by the desorption of chemisorbed oxygen (O<sup>2-</sup>)<sup>[19]</sup> on the surface of SnO<sub>2</sub> sensor.



Resistivity change of undoped SnO<sub>2</sub> may also result from incomplete oxidation of the film to stoichiometric SnO<sub>2</sub>. For the MO-doped sensors, the addition of 3 wt.% of TiO<sub>2</sub> to SnO<sub>2</sub> results in significantly increases of sensor resistivity. In general, the additions of a Group III element cause SnO<sub>2</sub> films resistivities to increase while the additions of a Group V element cause them to decrease<sup>[20-21]</sup>. However, large additions of a Group IV element, e.g. Sb, cause the films resistivity to increase, reversing the trend predicted by the controlled valency mechanism. The rise may be caused by gradual loss of crystallinity. In our case, the three additives are the same Group IV as SnO<sub>2</sub>. Thus, increase in resistivity might be due to the additions of such high temperature refractory materials. Inhibitory effect of the three metal

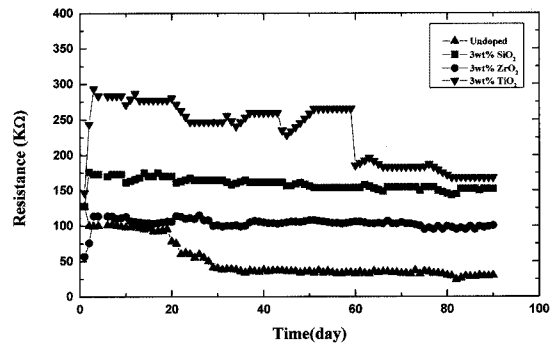


Fig. 6. Long-term resistance transient of MO-doped SnO<sub>2</sub> sensors at an operating temperature of 400 °C.

oxides on the sintering process retards initial structural stabilization during heating at 400 °C. 3 wt.% SiO<sub>2</sub>-doped SnO<sub>2</sub> sensor can reach a stabilized resistance only after 35 h heating but 3 wt.% TiO<sub>2</sub>-doped and 3 wt.% ZrO<sub>2</sub>-doped SnO<sub>2</sub> sensors exhibit the resistance stabilization in 38 h and 72 h, respectively. Melting temperatures<sup>[22]</sup> as an indirect indication of ability in diffusion or sintering between any constituent materials (extent of sintering) are respectively 1996 K, 2130 K, and 2950 K for SiO<sub>2</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub>. The stabilizing time increases in the order of SiO<sub>2</sub>-doped, TiO<sub>2</sub>-doped, and SiO<sub>2</sub>-doped SnO<sub>2</sub> sensors, corresponding to the same order of their melting temperatures. It could be suggested that all the three additives have retard active effect on sintering of SnO<sub>2</sub>.

Long-term resistance drifts are shown in Fig. 6. Just before contacting methane with the sensor surface for investigation of long-term sensitivities, the sensor resistances,  $R_a$ , were measured at an interval of 1 day.  $R_a$  of the undoped SnO<sub>2</sub> decreases continuously at the operating temperature of 400 °C. Continuous heating of the undoped SnO<sub>2</sub> sensor for at least 30 days is required to get structural stabilization if the sensor is working at 400 °C. The undoped SnO<sub>2</sub> sensor has the lowest resistivity compared to the MO-doped sensors. Tin as one of the Group IV elements has more metallic property than silicon, zirconium and titanium. As compared to the resistances of SiO<sub>2</sub> and ZrO<sub>2</sub> dopants, the TiO<sub>2</sub>-doped SnO<sub>2</sub> sensor has large fluctuations of  $R_a$ . However, the other two dopants provide relatively stabilized resistances of the SnO<sub>2</sub> sensor. Long-term resistant drifts may be related to phase transformation of one phase in a sensor material and change in oxidation state

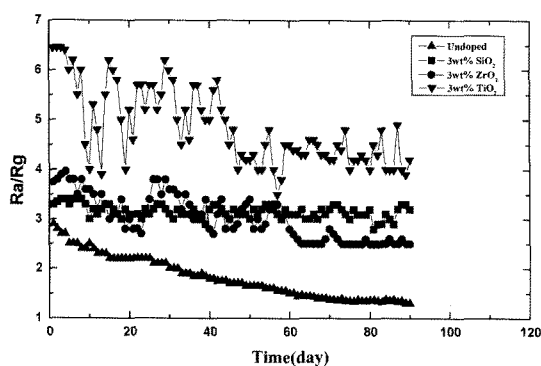


Fig. 7. Long-term CH<sub>4</sub> sensing characteristics of MO-doped SnO<sub>2</sub> sensors at an operating temperature of 400 °C.

by continuous heating at a high operating temperature. As discussed below, frequent contact with hydrocarbon gases for a long time causes the sensor surface to change oxide form. TiO<sub>2</sub> may be transformed into another oxide forms by frequent contact with methane as a reducing gas, resulting in large fluctuation of Ra.

The sensitivity is equal to the change in electrical resistivity when methane contacts the sensor surface. However, drift in resistance in air does not correspond to that in the test gas<sup>[23]</sup>. Long-term sensitivities to 5000 ppm CH<sub>4</sub> for MO-doped SnO<sub>2</sub> sensor continuously heated at an operating temperature of 400°C were measured up to 90 days at an interval of 1 day. Fig. 7 shows the long-term sensing characteristics for the MO-doped sensors compared with those of undoped SnO<sub>2</sub> sensor.

Although the resistance of the undoped SnO<sub>2</sub> sensor can stabilize in 30 days, its sensing characteristics do not be stabilized even when the sensor is operated up to 90 days. The TiO<sub>2</sub>-doped sensor exhibits the highest CH<sub>4</sub> sensitivity but has the largest fluctuating ripples of CH<sub>4</sub> sensitivity. Smaller but significant fluctuation in methane sensitivity is also shown in the ZrO<sub>2</sub>-doped sensor. CH<sub>4</sub> sensitivities for all the sensors except for the SiO<sub>2</sub>-doped one continuously drift downwards. CH<sub>4</sub> sensitivities for the SiO<sub>2</sub>-doped SnO<sub>2</sub> fluctuated only within  $\pm 5\%$  during continuous heating for 90 days. For the commercial stannic oxide gas sensors, either seasonal or environmental drifts or drifts resulting from contamination have been frequently encountered during long-term operation. Contamination drifts occur in the case of hydrogen and alcohol vapor detections under the atmospheric conditions of temperature over 40 °C and

RH over 80 %. The contamination drift caused by change in sensor surface structure and polymerization of a binder can be markedly improved by incorporating trace amounts of vanadium and rhenium into the sensor. It should be noted that in our experiment ethylene glycol is used as a binder and silicon is added to SnO<sub>2</sub> as the oxide form, differently from most commercial SnO<sub>2</sub> sensors with ethyl silicate binder. The long-term methane sensitivity fluctuation seems to be greatly dependent on structural stability and catalytic activity of additives in SnO<sub>2</sub><sup>[6]</sup>.

The sensor may easily experience change in surface morphology by heating at a high operating temperature, change in oxidation state by contacting with a reducing gas, and degradation of catalytic activity. Like our experimental case, frequently contact with a high concentration of a reducing gas such as 5000 ppm CH<sub>4</sub> causes the surface of the sensors to change valence state. In general, transition metals have many kinds of oxides. Titanium has many types of metal oxides such as TiO, Ti<sub>3</sub>O<sub>5</sub>, Ti<sub>2</sub>O<sub>3</sub>, Ti<sub>4</sub>O<sub>7</sub>, and TiO<sub>2</sub>. The most stable form is TiO<sub>2</sub> under a high oxygen partial pressure, for example, in the air. Zirconium also has various oxide forms such as ZrO, Zr<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>.

A more serious sensitivity drift arises from high methane sensitivity of these MO-doped sensors. As shown in Fig. 2, methane sensitivity is closely related to catalytic activity of the additives. Increase in methane sensitivity for 1 wt.% addition of TiO<sub>2</sub>, ZrO<sub>2</sub> and SiO<sub>2</sub> is, respectively, 0.20, 0.83 and 1.54. The decreasing order in methane sensitivity is 3 wt.% TiO<sub>2</sub>, 3 wt.% ZrO<sub>2</sub>, and 3 wt.% SiO<sub>2</sub>-doped SnO<sub>2</sub> sensors. TiO<sub>2</sub>-doped SnO<sub>2</sub> sensor exhibits the highest sensitivity but very large change in time-dependent response to 5000 ppm CH<sub>4</sub>. It should be noteworthy that titanium and zirconium as transition metals are included in a Group IVB element<sup>[24]</sup> while silicon is included in the same Group IVA as Sn. Therefore, TiO<sub>2</sub> and ZrO<sub>2</sub> can play an important role of catalysts for CH<sub>4</sub> oxidation. Sensitivity decreases as the hydrocarbon oxidation activity degrades during long-term operation. Furthermore, the ambient humidity can be measured by humidity TiO<sub>2</sub>-SnO<sub>2</sub> ceramic sensor<sup>[25]</sup>. Even if TiO<sub>2</sub> content in SnO<sub>2</sub> is high, the TiO<sub>2</sub>-SnO<sub>2</sub> sensor material is significantly moisture-sensitive. In Table 1, difference between the sensitivity at 30RH and at 70 % is listed.

3 wt.% TiO<sub>2</sub>-doped SnO<sub>2</sub> sensor has large RH de-

Table 1. Difference in 5000 ppm CH<sub>4</sub> Sensitivity between 30 % RH and 70 % RH for 3 wt.% MO-doped SnO<sub>2</sub> Sensors at an Operating Temperature of 400 °C.

Metal oxides	Condition	Sintering temperature		
		700 °C	750 °C	800 °C
		Humidity difference (%)		
SiO <sub>2</sub>	1 wt.%	1.150	1.255	1.248
	2 wt.%	1.673	1.429	1.780
	3 wt.%	1.833	2.004	1.931
ZrO <sub>2</sub>	1 wt.%	0.950	1.099	1.098
	2 wt.%	1.646	1.740	2.020
	3 wt.%	2.210	2.380	2.330
TiO <sub>2</sub>	1 wt.%	1.455	1.585	1.508
	2 wt.%	2.618	2.925	2.520
	3 wt.%	3.142	3.620	3.160

pendence, indicating that TiO<sub>2</sub> is an inappropriate material for SnO<sub>2</sub> sensor. The SiO<sub>2</sub>-doped SnO<sub>2</sub> sensor showing the lowest sensitivity among the three MO-doped sensors has highly stable long-term stability.

#### 4. Conclusions

TiO<sub>2</sub>, ZrO<sub>2</sub>, and SiO<sub>2</sub> were added to SnO<sub>2</sub> sensor to improve long-term stability. Short-term sensor resistances of the MO-doped SnO<sub>2</sub> sensors at 400 °C increase with time. The increase in resistivity might be due to inhibitory effect of the three metal oxides on retarding structural stabilization during the sintering process. Metallic oxides having higher melting temperature have longer time for the resistance stabilization. Long-term resistances measured at an interval of 1 day are significantly fluctuated for the TiO<sub>2</sub>-doped SnO<sub>2</sub> sensor. However, the other two dopants provide comparatively highly stabilized resistances of the SnO<sub>2</sub> sensor. Such long-term resistance drifts may be related to phase transformation of one phase in a sensor material and oxidation state by continuously measuring CH<sub>4</sub> sensitivity at a high operating temperature of 400 °C. Long-term sensitivities up to 90 days were also measured at an interval of 1 day. SiO<sub>2</sub>-doped SnO<sub>2</sub> sensor exhibits significantly stable sensitivity to 5000 ppm methane whereas the TiO<sub>2</sub>-doped sensor exhibits the highest but the largest fluctuating ripples of CH<sub>4</sub> sensitivity. Smaller but significant fluctuation in methane sensitivity was also shown in the ZrO<sub>2</sub>-doped sensor. Titanium and zirconium oxides including a Group IVB metallic constituent have various oxide forms. Frequent contacts with

a reducing gas such as methane change oxidation state on sensor surface for TiO<sub>2</sub>-doped and ZrO<sub>2</sub>-doped SnO<sub>2</sub> sensors, resulting in poor long-term sensing stability.

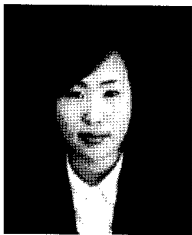
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