

## Solid Oxide Amperometric CO Sensor Prepared by DC Sputtering

Tatsumi Ishihara,<sup>1,2\*</sup> Toshikazu Mori,<sup>1</sup> Jun Iwata,<sup>1</sup> Hidehisa Hagiwara,<sup>1,2</sup> and Shintaro Ida<sup>1,2</sup>

<sup>1</sup>Department of Applied Chemistry, Faculty of Engineering, Kyushu University  
Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan

<sup>2</sup>International Institute for Carbon-Neutral Energy Research (WPI-I2CNER),  
Kyushu University, Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan

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An amperometric CO sensor using a solid oxide electrolyte was studied, and it was found that the oxygen pumping current increased with increasing CO concentration when Au(10 wt%)/In<sub>1.9</sub>Sn<sub>0.1</sub>O<sub>3</sub> and RuO<sub>2</sub>(10 wt%) were used for cathode and anode, respectively, and La<sub>0.9</sub>Sr<sub>0.1</sub>Ga<sub>0.8</sub>Mg<sub>0.2</sub>O<sub>3</sub> was used as the electrolyte. In this study, the electrode was prepared by DC sputtering. Although the morphology of the deposited electrode film was dense, the sensor responded sensitively to CO if the electrode was prepared by DC sputtering. Coating RuO<sub>2</sub>/La<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3</sub> powder on a RuO<sub>2</sub> electrode prepared by sputtering effectively increased sensitivity because of the increased surface area and oxidation activity, and a sensitivity to CO of ca. 19 μA/decade was achieved, which is ca. 4 times higher than that of powder painted electrodes (4.5 μA/decade) at 673 K in our previous study [Sens. Actuators, B **223** (2016) 535].

### 1. Introduction

A selective and reliable CO sensor is highly important in various areas because of safety issues due to the high toxicity of CO. Therefore, several types of CO sensor have been proposed, and some are already commercially available.<sup>(1)</sup> Among them, a semiconductor type sensor, namely, SnO<sub>2</sub> modified with additives, is widely used for monitoring CO in rooms,<sup>(2–6)</sup> and also solid electrolyte type sensors have also been widely studied.<sup>(7–12)</sup> However, the most serious issue with the semiconductor-type sensor is low selectivity. Therefore, catalytic combustion-type and electrochemical-type CO sensors are also widely used for detection of CO. In the case of electrochemical CO sensors, selective detection of CO can be achieved; however, maintenance of the sensor is required relatively often (at least once per year). Recently, the ability to detect CO in exhaust gas from a gas water heater has been strongly demanded after an accident caused by incomplete combustion. However, applying a semiconductor-type CO sensor which monitors the combustion state is very difficult, and there is an urgent requirement for the development of an alternative CO sensor that is highly selective and can detect CO directly in an exhaust gas line.<sup>(1)</sup>

To meet this demand, a CO sensor using a solid state electrolyte was proposed and studied intensively.<sup>(1)</sup> Solid electrolyte-type gas sensors generally have better selectivity for the gas species of interest. Therefore, an O<sub>2</sub> sensor using yttria-stabilized ZrO<sub>2</sub> has been widely used for

\*Corresponding author: e-mail: ishihara@cstf.kyushu-u.ac.jp

monitoring  $P_{O_2}$  in engine exhaust gas.<sup>(1)</sup> On the other hand, mixed potential type sensors have been attracting much attention recently because they offer a wider range of detectable gas species.<sup>(7)</sup> To date, there have been many reports on mixed potential-type sensors.<sup>(8–12)</sup> In our previous studies, we investigated the amperometric type sensor based on changes in the oxide ion pumping current in a  $LaGaO_3$ -based oxide, and high sensitivity as well as selectivity was exhibited by this type sensor against  $CH_4$ ,  $C_3H_6$ , and  $NO$  based on the choice of electrode catalyst.<sup>(13–17)</sup> The detection mechanism of this sensor was reported in our previous study.<sup>(14)</sup> However, we applied +1 V to the active electrode for oxidation, and oxygen was electrochemically pumped from the inactive to the active electrode to oxidize the sensed gas. Since the oxygen partial pressure on the active electrode was decreased by the oxidation reaction of the pumped oxygen, the driving force for oxygen pumping was increased, which caused the oxide ion current also to increase upon exposure to a gas like  $CO$ . We noted that the electrode overpotential of the active electrode decreased upon exposure to  $CO$ , which might have been caused by decreased  $P_{O_2}$  around the active electrode. This may be another reason for increased oxygen pumping current when the sensor was exposed to  $CO$ . In this study, we investigated the amperometric  $CO$  sensor based on the same detection mechanism,<sup>(17,18)</sup> i.e., a combination of active and inactive electrode catalysts for  $CO$  oxidation. The effects of electrode deposition by sputtering were studied along with miniaturization and reproducibility of the sensor.

## 2. Experimental Methods

A solid electrolyte of  $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$  (denoted as LSGM) was prepared by sintering LSGM powder, which was prepared using a conventional solid state reaction method.<sup>(19,20)</sup> The diameter and thickness of the disk were 17 and 0.4 mm, respectively, unless otherwise noted.  $RuO_2$  and  $Au/In_{1.9}Sn_{0.1}O_3$  (ITO) were deposited on each face of the LSGM disk by DC sputtering (Pascal Co. Ltd.). Dense disks of  $RuO_2$  and  $Au/ITO$  (10 wt%  $Au/In_{0.927}Sn_{0.073}O_{1.5}$ ) were used as the target of anode and cathode, respectively. Deposition of each electrode was performed at 773 K with 12 W constant power mode for 4 h. The deposited electrode was square with a 5 mm length. After deposition of electrodes, Pt lead electrodes were deposited on each by DC sputtering, and Pt lead lines were connected to the Pt lead electrodes using Pt paste followed by calcining at 873 K for 1 h. A schematic image of the prepared sensor element is shown in Fig. 1. To increase the sensitivity,  $RuO_2/La_{0.6}Sr_{0.4}CoO_3$  (LSC) (1:9) was painted on the sputtered  $RuO_2$  electrode. ITO and LSC were also prepared by the solid state reaction method using metal nitrates or oxides as starting chemical reagents. Before preparation of a slurry, the electrode powder was calcined at 873 K for 6 h.

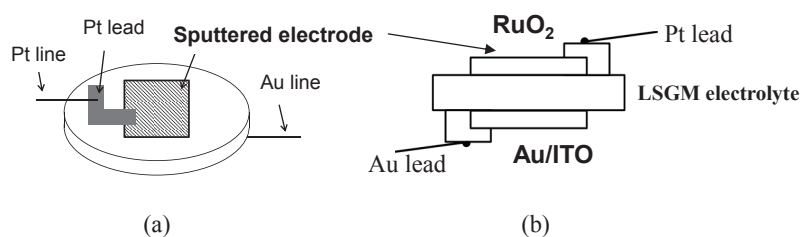


Fig. 1. Schematics of the prepared sensor element using  $Au/ITO$  and  $RuO_2$  electrodes: (a) top view and (b) cross-sectional view.

In the measurement assembly, the sensor element was placed in a gas flow chamber in which either reference air or sample CO (50–3000 ppm), which is made by mixing 1% CO in He with air, was fed at 100 ml/min. Change in current density was measured by the dc two-probe method, and Pt and Au wires were used as lead wires for the active and the inactive electrodes, respectively. Pt and Au meshes were also used as current correctors for the active and inactive electrodes, respectively, and were set on the lead electrode deposited by sputtering using commercial Pt and Au pastes. In the amperometric mode, 1 V dc was always applied using a potentiostat/galvanostat (Hokuto Denko HA301) as the RuO<sub>2</sub> based electrode was always positive. The voltage and current were measured with a digital multimeter (Advantest, Model R645A) and/or digital electrometer (Advantest, Model R8240). The sensitivity of the sensor was defined as a current change against the CO concentration of one order of magnitude. The sensing property was measured several times with several elements and the reproducibility of the sensitivity was confirmed (Deviation of sensitivity is within 5%).

### 3. Results and Discussion

Figure 2 shows scanning electron microscopy (SEM) images of Au/ITO electrodes prepared by DC and radio frequency (RF) sputtering. In both methods, an Au/ITO film was successfully deposited on an LSGM film, and EDX analysis suggested that the composition of the film was almost the same as 10 wt%/In<sub>1.9</sub>Sn<sub>0.1</sub>O<sub>3</sub>. However, the morphology of the electrode differed between DC and RF sputtering. As shown in Fig. 2, a more dense and smooth morphology of the Au/ITO electrode was obtained by DC sputtering compared with that from RF sputtering. A tighter contact was also achieved on the Au/ITO electrode deposited by DC sputtering. Therefore, we used DC sputtering for preparation of the Au/ITO and RuO<sub>2</sub> electrodes.

Figure 3 shows SEM images of the fractured surface of Au/ITO and RuO<sub>2</sub> electrodes. It is obvious that flat and uniform thicknesses of electrodes were deposited successfully by DC sputtering. Although a small gap was observed on the Au/ITO electrode, this could have been formed when fracturing the surface. The thickness of the deposited electrode was estimated to be

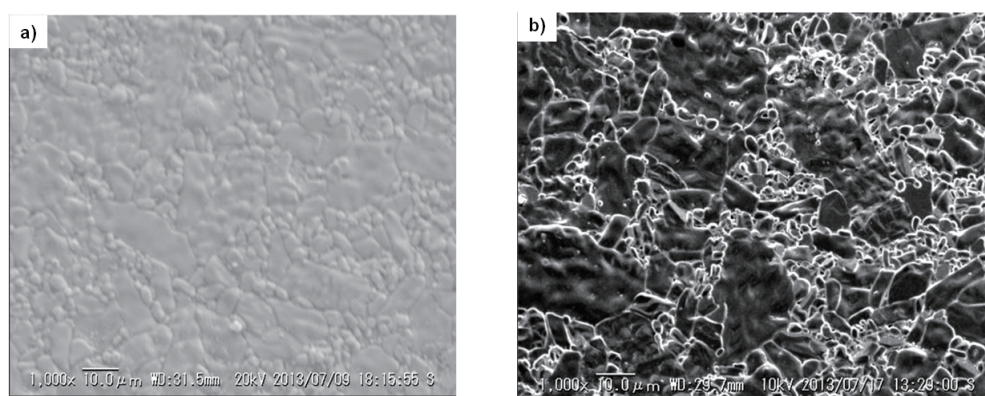


Fig. 2. SEM images of Au/ITO electrodes prepared by (a) DC and (b) RF sputtering.

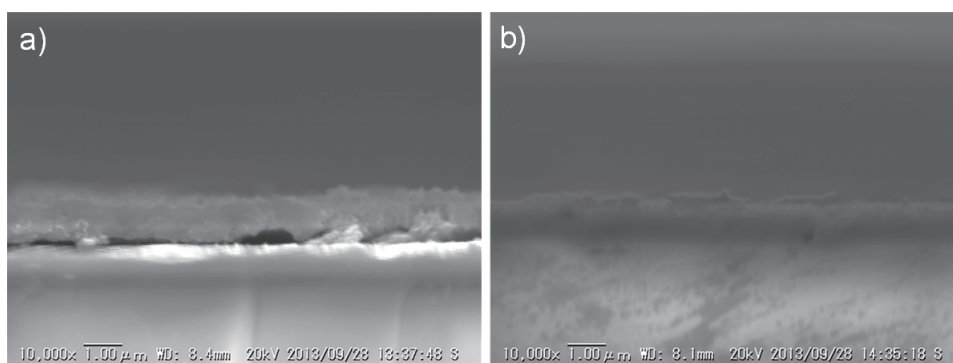


Fig. 3. SEM images of the fractured surface of (a) Au/ITO and (b) RuO<sub>2</sub> electrodes.

ca. 1mm for both Au/ITO and RuO<sub>2</sub> electrodes. It is also noted that a dense film was deposited on both electrodes in spite of the columnar shape that tends to be deposited in sputtering.

Figure 4 shows typical responses to CO at 773 K on the sensor with RuO<sub>2</sub> and Au/ITO film electrodes. Obviously, oxygen pumping current was increased upon exposure to CO, and the change in current increased with increasing CO concentration. The increase in current upon exposure to CO on the sensor using the electrode deposited by sputtering is the same as that using Au/ITO and RuO<sub>2</sub>/LSC prepared using the powder painting method. Therefore, the detection mechanism seems to be the same for both sensors. Figure 5 shows the current change of the sensor as a function of CO concentration at temperatures from 573 to 773 K. At each temperature, it is obvious that oxygen pumping current increased with increasing CO concentration, so CO can be detected by observing the oxygen pumping current. The sensitivity to CO increased with increasing operating temperature, and at 773 K, a sensitivity of 93.2 μA/decade to CO was achieved. This sensitivity is 10 times larger than that of the sensor prepared by hand painting in our previous study.<sup>(21)</sup> In Fig. 5, the reproducibility of the sensor data is also shown, and it is obvious that reproducibility of the sensor is reasonably high. Considering the sensitivity, higher operating temperatures are suitable; however, even at 673 K, it is obvious that reasonable linearity was observed between oxygen pumping current and CO partial pressure.

In our previous study, this type sensor was highly selective to CO; however, only oxygen strongly affects the oxygen pumping current. Therefore, the influence of oxygen on this sensor with electrodes deposited by sputtering was studied. Figure 6 shows the response to O<sub>2</sub> of the sensor at 673 K. Upon exposure to low partial pressure of oxygen, current was immediately decreased and then gradually increased. When the atmosphere was returned to air, the current returned to the original level after the overshoot. Impedance measurements suggested that this decrease in oxygen pumping current was caused by an increased overpotential of the Au/ITO electrode. However, the change in current due to O<sub>2</sub> was not large for the sensor using Au/ITO and RuO<sub>2</sub> electrodes prepared by sputtering. The current is shown in Fig. 6(b) as a function of oxygen partial pressure. In this figure, current change in response to O<sub>2</sub> at 773 K is also shown. At 773 K, dependence of current change on P<sub>O<sub>2</sub></sub> was not large, particularly, in a P<sub>O<sub>2</sub></sub> range higher than 10%, which is the expected P<sub>O<sub>2</sub></sub> range for combustion control in small steam boilers. In contrast, at 773 K, sensitivity to O<sub>2</sub> was greatly increased (404 μA/decade), so the optimum operating temperature for this sensor could be around 673 K.

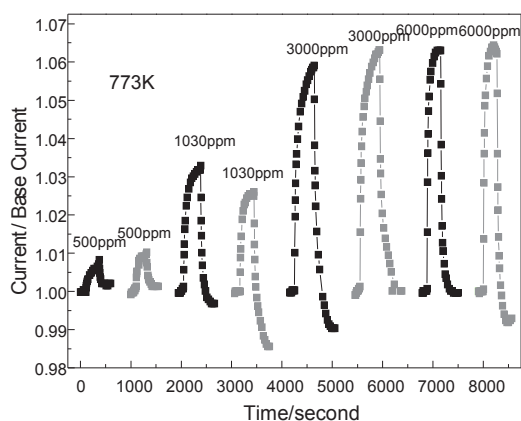


Fig. 4. Typical response to CO at 773 K on the sensor with RuO<sub>2</sub> and Au/ITO film electrodes. Black is the first response, and gray indicates the second trial for reproducibility.

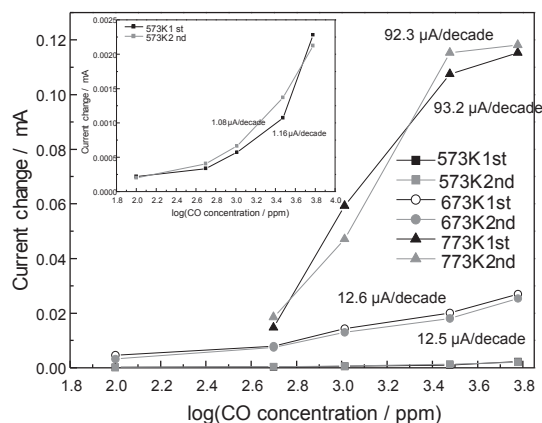
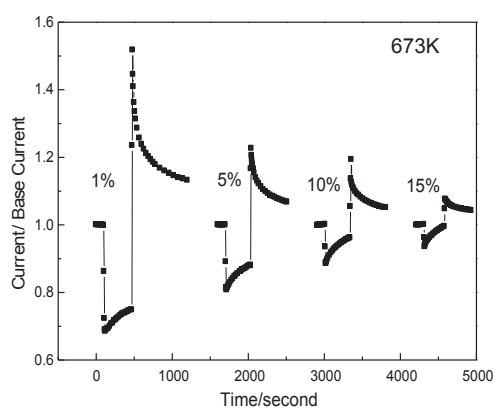
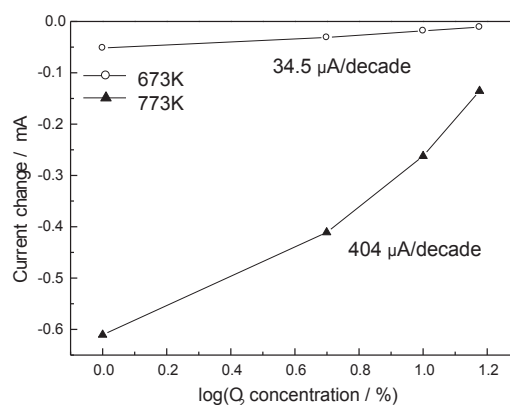


Fig. 5. Change in current of the sensor using Au/ITO and RuO<sub>2</sub> as a function of CO concentration at temperatures from 573 to 773 K. “1st” means response in the first trial, and “2nd” means response in the second trial for reproducibility.



(a)



(b)

Fig. 6. (a) Response to O<sub>2</sub> on the sensor at 673 K and (b) change in current of the sensor as a function of oxygen partial pressure from 573 to 773 K.

To increase sensitivity to CO, coating the RuO<sub>2</sub> electrode with RuO<sub>2</sub>/LSC powder was investigated. A schematic image of the sensor is shown in Fig. 7. A powder of RuO<sub>2</sub>/LSC was hand-painted on the Pt lead wire deposited on the RuO<sub>2</sub> film electrode. After coating, the sensor was calcined at 873 K for 30 min before measurement. Figure 8(a) shows a typical response curve to CO for this sensor at 773 K. It is obvious that the oxygen pumping current was increased and returned to its original level within 60 s after expose to CO and air. Therefore, considering the time required to exchange the atmosphere in the measurement chamber, the response of this sensor was reasonably fast. We also observed that the change in oxygen pumping current increased with increasing CO partial pressure. However, at 6000 ppm CO, which is an excessively high

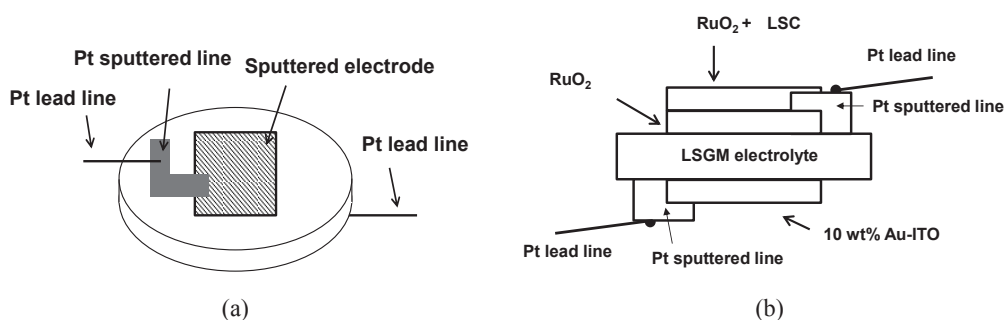


Fig. 7. Schematics of the sensor with RuO<sub>2</sub>/LSC powder coated on RuO<sub>2</sub>: (a) top view and (b) cross-sectional view.

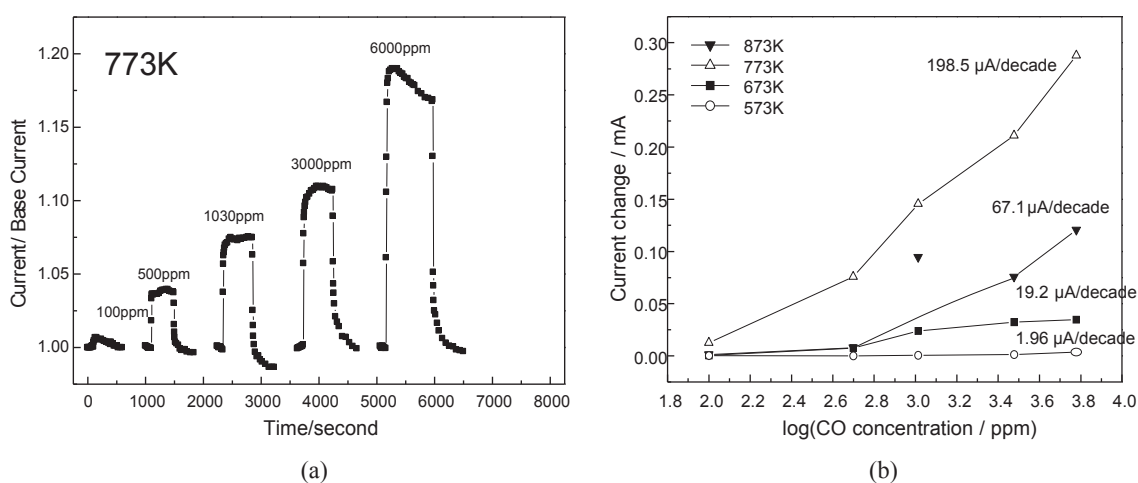


Fig. 8. (a) Typical response curve to CO of the sensor using RuO<sub>2</sub>/LSC-coated RuO<sub>2</sub> and Au/ITO electrodes at 773 K. (b) Oxygen pumping current as a function of CO from 673 to 873 K.

concentration, the current achieved a maximum and gradually decreased with time, i.e., the so-called annealing phenomena in the response was observed. This may be explained by the reaction of CO with the active oxygen initially existing on the surface of the RuO<sub>2</sub> film electrode followed by using oxygen, which was supplied by the electrochemical pump. The relationship between oxygen pumping current and CO partial pressure of the sensor using the RuO<sub>2</sub>/LSC powder-coated RuO<sub>2</sub> film electrode is shown in Fig. 8(b). Obviously, the oxygen pumping current monotonically increased with increasing CO concentration. Compared to the slopes of lines in Fig. 5, those in Fig. 8 are much larger at all operating temperatures, and this suggests that the sensitivity of the sensor can be increased by coating the RuO<sub>2</sub> film electrode with RuO<sub>2</sub>/LSC powder. For example, the sensitivity to CO at 673 K was increased from 12.6 to 19.5  $\mu\text{A}/\text{decade}$ . Although contact between RuO<sub>2</sub> electrode was greatly improved by preparing it using sputtering, the surface area was much smaller than that of the powder-coated one. Therefore, by coating with RuO<sub>2</sub>/LSC powder, reaction sites for CO oxidation can be increased, resulting in increased sensitivity to CO. At 973 K, an oxidation reaction also occurred on Au/ITO, the inactive electrode. Therefore, the difference in P<sub>O<sub>2</sub></sub> between anode and cathode became smaller at excessively high operating temperatures. In any

case, it is clear that the oxygen pumping current of the sensor with RuO<sub>2</sub> and Au/ITO film prepared by sputtering can be used for detection of CO in exhaust gas. Because it is expected that the miniaturization of the sensor may also be easily achieved, reasonable response and high sensitivity of the sensor prepared with sputtering is highly attractive.

#### 4. Conclusion

This study revealed that the oxygen pumping current increased with increasing CO concentration when Au(10 wt%)/ITO and RuO<sub>2</sub>(10 wt%) were used for cathode and anode, respectively, and LSGM was used as the electrolyte. In this study, electrodes were prepared by DC sputtering and their sensitivity to CO was much improved by good contact between electrolyte and electrode. Although the morphology of the deposited electrode film was somewhat dense, the oxygen pumping current in the sensor responded sensitively to CO. Coating RuO<sub>2</sub>/LSC powder on RuO<sub>2</sub> electrodes prepared by sputtering is effective for increasing sensitivity to CO and, considering the sensitivity to O<sub>2</sub>, the optimum operating temperature seems to be 673 K.

#### References

- 1 N. Docquier and S. Candel: *Prog. Ener. Combust. Sci.* **28** (2002) 107.
- 2 B. Bahrami, A. Khodadadi, M. Kazemeini, and Y. Mortazavi: *Sens. Actuators, B* **133** (2008) 352.
- 3 L. I. Trakhtenberg, G. N. Gerasimov, V. F. Gromov, T. V. Belysheva, and O. J. Ilegbusi: *Sens. Actuators, B* **209** 562 (2015).
- 4 C. J. Li, M. Lv, J. L. Zuo, and X. T. Huang: *Sensors* **15** (2015) 3789.
- 5 N. Miura, K. Kanamaru, Y. Shimizu, and N. Yamazoe: *Solid State Ionics* **40–41** (1990) 452.
- 6 T. Hibino, A. Hashimoto, S. Kakimoto, and M. Sano: *J. Electrochem. Soc.* **148** H1 (2001).
- 7 N. Miura, G. Lu, and N. Yamazoe: *Solid State Ionics* **136–137** (2000) 533.
- 8 E. L. Brosha, R. Mukundan, D. R. Brown, F. H. Garzon, and J. H. Visser: *Solid State Ionics* **148** (2002) 61.
- 9 J. W. Fergus: *Sens. Actuators, B* **122** (2007) 683.
- 10 J. Wang, P. Elumalai, D. Terada, M. Hasei, and N. Miura: *Solid State Ionics* **177** (2006) 2305.
- 11 Y. Shimizu, H. Nishi, H. Suzuki, and K. Maeda: *Sens. Actuators, B* **65** (2000) 141.
- 12 N. Miura, T. Raisen, G. Lu, and N. Yamazoe: *Sens. Actuators, B* **47** (1998) 84.
- 13 A. Dutta and T. Ishihara: *Mater. Manuf. Process.* **21** (2006) 225.
- 14 A. Dutta, T. Ishihara, and H. Nishiguchi: *Chem. Mater.* **16** (2004) 5198.
- 15 A. Dutta and T. Ishihara: *Electrochem. Solid-State Lett.* **8** (2005) H46.
- 16 A. Dutta and T. Ishihara: *Sens. Actuators, B* **108** (2005) 309.
- 17 A. Dutta, H. Nishiguchi, Y. Takita, and T. Ishihara: *Sens. Actuators, B* **108** (2005) 368.
- 18 C. Phawachalotorn, O. Sanguanruang, and T. Ishihara: *Sens. Actuators, B* **161** (2012) 635.
- 19 T. Ishihara, H. Matsuda, and Y. Takita: *J. Am. Chem. Soc.* **116** (1994) 3801.
- 20 T. Ishihara, H. Minami, H. Matsuda, H. Nishiguchi, and Y. Takita: *Chem. Comm.* (1996) 929.
- 21 T. Ishihara and J. Iwata: *Sens. Actuators, B* **223** (2016) 535.