

## A Novel Surface Modification of SnO<sub>2</sub>-Based CO Gas Sensors to Improve Temperature and Humidity Dependence

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A significant improvement in temperature and humidity dependence of SnO<sub>2</sub>-based CO gas sensors has been achieved by a novel surface modification with sulfuric acid, thiourea, ruthenium, and rhodium.

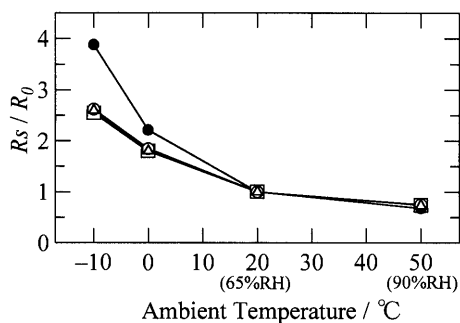
We have recently demonstrated that surface modification of a SnO<sub>2</sub>-based CO gas sensor with sulfuric acid or thiourea solution notably enhances the sensitivity to CO, the selectivity against H<sub>2</sub>, and the long-term stability.<sup>1,2</sup> This surface modification is simply accomplished by dipping the sensor element in a dilute sulfuric acid or thiourea solution for only a few seconds, then heating it at 600 °C for 5 min. The results suggested a new concept of the sensor modification that the sensing properties could be drastically changed by the surface treatment of the sintered sensor element using a similar procedure. In this study, we have examined the same surface modification method substituting a metal salt solution containing platinum group metal, such as ruthenium and rhodium, for sulfuric acid or thiourea solution to improve the temperature and humidity dependence of the SnO<sub>2</sub>-based CO sensor. The temperature and humidity dependence of the sensor's sensitivity is known to be a major disadvantage for detecting CO as well as other reducing gases.<sup>3-5</sup> However, the practical solution for this problem has not yet been found. Use of platinum group metals for resolving this matter was initially suggested by the fact that the sensitivity to water vapor of a SnO<sub>2</sub>-based gas sensor was reduced by doping the SnO<sub>2</sub> with a small amount of palladium.<sup>6</sup> As a consequence, this paper reports the remarkable effects of the surface modification with ruthenium and rhodium on the CO sensing properties against temperature and humidity changes. A combination of the surface modification with the platinum group metals and that with sulfuric acid and thiourea is also shown to further improve the temperature and humidity dependence and to induce excellent long-term stability.

The preparation procedure of a sensor element, consisting of 2 wt% Pd-doped SnO<sub>2</sub> and alpha-alumina with two Ir-Pd alloy coils, was the same as that previously described.<sup>1,2</sup> The surface modification of the sensor element was performed by dipping the sensor element in a metal salt solution for 2 sec., drying for 3 min., and heating at 600 °C for 5 min. The metal salt solution containing RuCl<sub>4</sub>·5H<sub>2</sub>O or RhCl<sub>3</sub>·4H<sub>2</sub>O or both salts was used for the surface modification with ruthenium or rhodium or a combination of both metals, respectively. Sensor resistance measurements were carried out using an environmental test chamber (Tabai Espec Model PR-2G), in which the temperature and humidity was automatically controlled, following a programmed sequence: 20 °C, 65 %RH (1st step); 0 °C (2nd step); -10 °C (3rd step); 20 °C, 65 %RH (4th step); 50 °C, 90 %RH (5th step); 20 °C, 65 %RH (final step). For example, when fresh

air controlled at 20 °C and 65 %RH with a test gas (100 ppm CO) was introduced into the chamber, the gas inlet and outlet of the chamber were closed. Then the chamber was left for 3 to 12 hours (depending on the step), until the desirable temperature and humidity were accomplished. Thirty minutes after the atmosphere in the chamber had reached the desirable conditions, the sensor resistance was measured: then the chamber was evacuated. This process was repeated in the following steps. With the above sequence, a wide range of relative humidity, from 0 to 90 %RH, was employed. During the sensor resistance measurement, pulsed voltage was applied between the two coils of the sensor element so as to switch the element temperature between 80 °C (90 s) and 280 °C (60 s).<sup>7</sup> The sensor resistance between the two coils was measured at the end of the low temperature period. The sensor resistance was evaluated with the average value of 10 sensor elements. The deviation from the average value was within ± 10 %.

Experiments on the modifications of the sensor surface with ruthenium and rhodium were undertaken to investigate the dependence of the sensor resistance in CO relative to the concentration of the metal salt solution. The sensor resistances in 100 ppm CO at 20 °C and 65 %RH of the sensors modified using the solutions separately containing 0.001 mol dm<sup>-3</sup> RuCl<sub>4</sub>·5H<sub>2</sub>O and 0.001 mol dm<sup>-3</sup> RhCl<sub>3</sub>·4H<sub>2</sub>O were 20.6 kΩ and 4.4 kΩ, respectively, while that of the unmodified sensor was 6.7 kΩ. However, increasing concentration of the surface modification with the platinum group metal resulted in the drastic increase in sensor resistance; the sensor resistance changed to several MΩ at 0.1 mol dm<sup>-3</sup> for each case. This resistance change by the surface modification is undesirable, since accordingly the sensitivity to CO decreases at higher concentrations. Limitation of the concentration was also observed at the upper limit of the sensor resistance in 100 ppm CO for a SnO<sub>2</sub>-based CO gas sensor in practical use (25 kΩ for the sensor examined in this study). Therefore, we decided the concentration of the metal salt solution to be 0.001 mol dm<sup>-3</sup> for the subsequent experiments.

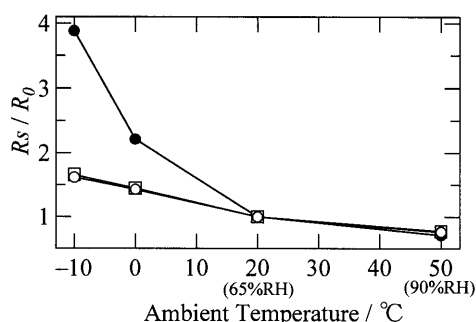
Figure 1 shows the temperature and humidity dependence of the sensor resistance of unmodified and modified sensors in 100 ppm CO. In this figure, the sensor resistance,  $R_s$ , is normalized with that in 100 ppm CO at 20 °C and 65 %RH,  $R_0$ , for each case. For the reason mentioned above, the surface modification with ruthenium or rhodium was performed using the solution containing 0.001 mol dm<sup>-3</sup> RuCl<sub>4</sub>·5H<sub>2</sub>O or 0.001 mol dm<sup>-3</sup> RhCl<sub>3</sub>·4H<sub>2</sub>O, respectively. Solution containing 0.0005 mol dm<sup>-3</sup> RuCl<sub>4</sub>·5H<sub>2</sub>O and 0.0005 mol dm<sup>-3</sup> RhCl<sub>3</sub>·4H<sub>2</sub>O was also used to investigate the surface modification with a combination of both metals. The resistance of the unmodified sensor increased with decreasing temperature and humidity, indicating that the sensitivity to CO is reduced with lower temperature and humidity. However, a comparison between the unmodified and



**Figure 1.** Temperature and humidity dependence of the sensor resistance,  $R_s$ , in 100 ppm CO for the  $\text{SnO}_2$ -based sensors unmodified (●) and modified with ruthenium (○), rhodium (△), and with both metals (□).  $R_0$ : 6.7 k $\Omega$  (●), 20.6 k $\Omega$  (○), 4.4 k $\Omega$  (△), 17.9 k $\Omega$  (□).

modified sensors clearly indicates that ruthenium and rhodium each acts to restrain the increase in sensor resistance with lowering temperature and humidity. Notably, the sensor resistance at low temperature and humidity was reduced equally (*i.e.*, to the same level) by the surface modifications with these metals. The mechanism of the improvement in the temperature and humidity dependence by the surface modification is unknown at present. However, it is a valuable finding that the sensor surface modified with ruthenium and/or rhodium by the method developed in this study decreases the sensor's sensitivity to variations in temperature and humidity.

Considering the remarkable effects of surface modifications with sulfuric acid and thiourea on the sensing properties of a  $\text{SnO}_2$ -based CO gas sensor,<sup>1,2</sup> a combination of the surface modifications with sulfuric acid and thiourea and that with the platinum group metals was also examined. In this case, the solution containing 0.0005 mol dm<sup>-3</sup>  $\text{RuCl}_4 \cdot 5\text{H}_2\text{O}$  and 0.0005 mol dm<sup>-3</sup>  $\text{RhCl}_3 \cdot 4\text{H}_2\text{O}$  was tried to use for the surface modification with the platinum group metals. In accordance with the previous results,<sup>1,2</sup> the surface modification with sulfuric acid or thiourea was carried out using 0.04 mol dm<sup>-3</sup> sulfuric acid or 0.1 mol dm<sup>-3</sup> thiourea solution, respectively. Both sulfuric acid



**Figure 2.** Temperature and humidity dependence of the sensor resistance,  $R_s$ , in 100 ppm CO for the  $\text{SnO}_2$ -based sensors unmodified (●) and modified with sulfuric acid, thiourea, ruthenium, and rhodium after 5 days (○) and 215 days (□).  $R_0$ : 6.7 k $\Omega$  (●), 2.2 k $\Omega$  (○, □).

and thiourea treatments were used in combination and applied serially, preliminary to the surface modification with the platinum group metals. The temperature and humidity dependence of the sensor subjected to this mixed surface modification is displayed in Figure 2. In this figure, the temperature and humidity dependence of the modified sensor after a long-term operation of 215 days is also presented. Based on a comparison of the results shown in Figures 1 and 2, it can be understood that the variation in the sensor resistance with temperature and humidity is further suppressed by the preliminary surface modifications with sulfuric acid and thiourea. This implies that the sulfuric acid and thiourea treatments are able to modify the sensor surface such that it is less sensitive to changes in temperature and humidity. In fact, this was successfully supported by the experiments of temperature and humidity dependence of the sensor modified with sulfuric acid and thiourea. The results revealed that the sulfuric acid and thiourea treatments each played a role to prevent the sensor resistance change with temperature and humidity, and that this effect was more enhanced for the sensor modified serially (*i.e.*, with sulfuric acid then with thiourea), compared to that modified with either of them, individually.

It is also demonstrated from Figure 2 that the improved temperature and humidity dependence of the modified sensor is maintained over 200 days. This proves that the preliminary surface treatments with sulfuric acid and thiourea stabilize the temperature and humidity dependence, and the effect of the mixed surface modification would continue during long-term operation. Therefore, it can be stated that the stabilization effects of the sulfuric acid and thiourea treatments to the sensor element are maintained even in the case that the surface modification with ruthenium and rhodium is subsequently performed. The most significant and valuable result revealed in this study is that the individual effects of the surface modifications using each of the platinum group metals, sulfuric acid, and thiourea are superimposed without negative interaction when these surface modifications to the sensor element are sequentially carried out. Thereby, notable improvement in the temperature and humidity dependence and in the stability of the  $\text{SnO}_2$ -based CO gas sensor has been attained, which finding is of practical value.

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