Planar resistive type SO2 sensors based on V2O5/WO3/TiO2 (VWT) have been reported to respond well to SO2 but with large cross-effects of NO and NH3. In this study, we added a porous Pt/alumina cover layer on a VWT film in order to decrease the cross sensitivities. The sensor response to SO2 is hardly affected by the Pt/alumina layer in the case of VWT sensor with 3.0 wt % V2O5 with Au electrodes, while the Pt/alumina layer affects the response of other VWT sensors. The VWT sensor (3.0 wt % V2O5) with Au electrodes with the porous Pt/alumina cover layer shows much smaller responses to CO, H2, H2O, NH3, and NO compared with the sensor without Pt/alumina cover layer. The porous Pt/alumina cover layer has a potential to improve the selectivity of the VWT sensor.

Key-words : Sulfur dioxide, Gas sensor, High temperature, Thick film, Catalyst layer, Platinum

1. Introduction

Today, coal is a very important fuel in addition to renewable energies. This is because the identified coal reserves are expected to last for 150 years, in contrast to oil and natural gas reserves, which may last for only 41 and 65 years, respectively. Furthermore, the cost of coal is approximately 1/6 of that of oil and natural gas. Therefore, it is predicted that coal consumption will increase by 2.5% per year in the range of 2003 to 2030 and it will continue to play an important role through the 21st century.

Coal, however, faces significant environmental challenges, since exhaust gas from coal combustion contains emissions such as SO2, NOx, etc. For instance, the exhaust gas from coal-fired kilns, flue gas, and stack gas include 300–500 ppm, 500–4000 ppm, and 5–10% of SO2, respectively. For SO2 monitoring and control in these conditions, SO2 sensors have to be made of very stable materials. To meet these conditions, Izu et al. reported on a planar SO2 sensor based on thick-films of V2O5/WO3/TiO2 (abbreviated VWT), since VWT shows a proven stability in sulfur oxide-rich combustion exhausts.

In Ref. 4), the resistive type VWT SO2 sensor has been reported to have a good response to SO2. However, it responded markedly to NO and NH3, which means the SO2 sensor has a strong cross-sensitivity to NO and NH3. This needs to be resolved.

In this study, we added a porous Pt/alumina cover layer on the VWT SO2 sensing film for the purpose of the decrease of the response to NO or NH3, and investigated responses to SO2 and other gases including NO and NH3.

2. Experimental

First, typical alumina substrates for thick-film technique (96% Al2O3) were prepared. On the front side of the alumina substrate, Pt or Au interdigital electrodes with a line and space definition of 100 μm each were screen-printed and fired, and a platinum heater was screen-printed and fired on the back side. Then, the sensor layers were fabricated. V2O5/WO3/TiO2 (abbreviated VWT, supplied by Argillon GmbH) was used as a sensing material. The V2O5 concentration was 1.5 or 3.0 wt % and the WO3 concentration was ca. 8–10 wt %. In this study, x%V2O5 is an abbreviation denoting the composition x wt % V2O5/8–10 wt % WO3/TiO2, in which x is 1.5 or 3.0. The VWT powders were added into an organic binder to prepare screen-printable pastes. Afterwards, the pastes were screen-printed on the alumina substrates with the electrodes and were fired at 700°C for 20 min.

Next, a porous Pt/alumina layer was fabricated as follows: An alumina powder was dispersed into a Pt(NH3)4Cl2 aqueous solution with the weight ratio of Pt/alumina = 1:99 and a dispersion was obtained. The dispersion was dried, and the dried Pt/alumina was heated in 5%H2 in N2 at 450°C. To make a screen-printing paste of Pt/alumina, the heated Pt/alumina powder was added into an organic binder. The paste of Pt/alumina was printed on a VWT layer and fired at 600°C for 40 min in air to form a porous and electrically insulating cover layer. The Pt/alumina layer had a thickness of 100–150 μm with a rough surface.

The sensors were heated by the back-side heater when the sensing properties were measured. The temperature was controlled by utilizing the relationship between heater resistance as determined in four-wire-technique and temperature, which had been calibrated before by using an infrared pyrometer.

In order to investigate its sensing properties, the sensor devices were placed into a test chamber, parallel to the gas flow. The resistance between the electrodes, which is the output of the sensors, was measured by a two-wire-method with a digital multimeter (Keithley 2700 series). The total gas flow amounted to either 1 or 5 L/min. We confirmed that the resistance of the sensor was independent of the total gas flow ratio. As a base gas, compressed air was used to measure the response to SO2, while a gas mixture of 20% O2 and N2 was used in the case of the response measurement towards other gases like CO, CO2, C2H6, H2O, H2, NO, and NH3.

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We defined the response value \( S \) in accordance to Eq. (1): 
\[
S = \frac{(R_0 - R)}{R_0}
\]  
\( R_0 \) stands for the resistance measured in base gas and \( R \) is the resistance in presence of the analyte.

3. Results and discussion

First, we checked the response curves of the VWT sensors when the \( \text{SO}_2 \) concentration was varied. In Fig. 1, the obtained results are shown. Figures 1(a) and 1(b) are resistance plots of the VWT sensors using Pt electrodes and Au electrodes, respectively. Not depending on the type of electrodes, the resistance of the 1.5\%VWT sensors is higher than that of the 3.0\%VWT sensors. In both cases using Pt and Au electrodes, the resistance of the VWT sensors with the added porous Pt/alumina layer is higher than the one of the VWT sensors without the additional porous cover layer. The resistance increase with an added porous Pt/alumina layer may be attributed to the decrease of the vanadium content in the VWT layer during adding the Pt/alumina cover layer.

The resistance difference with and without the Pt/alumina layer is smaller with Pt electrodes than with Au electrodes. From this result, it is considered that the vanadium concentration of the VWT layer on Pt electrodes already decreased due to the interaction between the VWT layer and the Pt electrodes before adding the Pt/alumina layer. This may be the reason of the small increase of the resistance of the VWT layer on the Pt electrodes when adding the porous Pt/alumina cover layer.

In contrast to that, before adding the Pt/alumina layer, the vanadium concentration in the VWT layer on Au electrodes might be almost the same as in the initial concentration. After adding the Pt/alumina layer, the vanadium concentration may decrease due to the interaction between the Pt and the VWT layer. We assume that this is the reason for the large difference of the resistance by adding the porous Pt/alumina cover layer. The details of the mechanism of the vanadium concentration decrease due to the existence of Pt need further consideration in future work.

In the case of the sensors with the porous Pt/alumina cover layer, the base line shifts are observed as soon as \( \text{SO}_2 \) is added, i.e., when the concentration is varied from 0 to 20 ppm, except for 3.0\%VWT sensors using Au electrodes. Especially, in the case of 1.5\%VWT sensors with the porous Pt/alumina cover layer using Au or Pt electrodes, the resistance decreases followed by a large increase of the resistance. This phenomenon has been also reported in the case of potentiometric type sensors using VWT.\(^3\) At the present stage, we cannot clarify whether there is a relationship between the results obtained in this study and the reported phenomenon of the potentiometric type sensors.\(^3\) However, this phenomenon occurs after adding the Pt/alumina layer. Alumina is used as a substrate even before adding the Pt/alumina layer. Thus, Pt affects the response of the sensor. Pt may be a key factor to clarify the mechanism.

The response behavior of 3.0\%VWT sensors using Au electrodes with the Pt/alumina layer is almost the same as that without the Pt/alumina layer, except for the response time. During the first exposure to \( \text{SO}_2 \) [3.0\%VWT: \( t = 30–70 \text{ min} \) in Fig. 1(b), the baseline shifted. However, the magnitude of the baseline shift became smaller at the second exposure. At the third exposure to \( \text{SO}_2 \), the baseline shift was hardly observed. Therefore, it was clarified that some \( \text{SO}_2 \) exposures prevented the baseline shift in the case of the 3.0\%VWT sensors using Au electrodes with the Pt/alumina layer.

Figure 2 shows the relationship between the sensor response, \( S \), of 3.0\%VWT sensors with Au electrodes and \( \text{SO}_2 \) concentration. The sensor response of 3.0\%VWT sensors using Au electrodes with the Pt/alumina layer is the same as that without
Pt/alumina layer, that is, the Pt/alumina cover layer does not affect the sensor response in the case of 3.0\% VWT sensors using Au electrodes.

Figure 3 shows sensor response curves of a 3.0\% VWT sensor with Au electrodes and a Pt/alumina cover layer between 400 and 550°C. The response decreases with increasing operating temperature. This tendency is the same as for a 3.0\% VWT sensor with Au electrodes but without the Pt/alumina layer.4)

Figure 4 shows the O2 dependency of the sensor response of 3.0\% VWT sensors with Au electrodes at 400°C. It is noteworthy to emphasize that the oxygen dependency of the sensor response decreases markedly with the porous Pt/alumina cover layer.

Figure 5 summarizes in a radar plot the sensor responses towards various possibly interfering gases. The sensor response to CO, H2, H2O, NH3, and NO decrease largely by with the added porous Pt/alumina layer, while the response value to C3H8 increases a little.

It is reported that NO changes to NO2 in the presence of a Pt catalyst, especially at low temperatures.6,7) Thus, a part of NO molecules might be oxidized to NO2 in the Pt/alumina layer. In the case of NO2, the VWT sensors respond in the other direction compared with the case of NO.9) This may be the reason of small response to NO in the case of the sensor with the Pt/alumina layer. It is well known that NH3,9) CO12),13) and H214),15) are oxidized on the surface of a Pt catalyst. This is considered to be the reason why the response values to NH3, CO, and H2 decrease when the Pt/alumina cover layer is added. The response decrease to H2O after adding the Pt/alumina layer might be attributed to the water adsorption on alumina particles in the Pt/alumina layer.16)

At the moment, the reason for the response increase towards propane is not clear, but a similar behavior occurs for platinum loaded zeolite covers on resistive hydrocarbon gas sensors.17) One interpretation is as follows: A part of the propane molecules is partly oxidized on the Pt catalyst of the Pt/alumina layer, and then CO and hydrocarbon such as methanol, ethanol, and/or acetone are formed. Thus, the molecule number of CO and hydrocarbons increases more than that of propane. In addition, this newly formed hydrocarbon species may be more reactive than the saturated hydrocarbon propane at these low temperatures. If this assumption was true and we cover the sensing layer with a thicker Pt/alumina layer, we would decrease the response to propane, since propane molecules are fully oxidized to CO2 and H2O.
4. Conclusions

To improve the selectivity of VWT-based SO$_2$ sensors, we covered the sensing layer with a porous Pt/alumina layer. As a result, no difference in the response of sensors based on 3.0% VWT with Au electrodes between sensors with and without an additional porous Pt/alumina cover layer was observed, but the cross-effects towards NO and NH$_3$ decreased with this additional porous Pt/alumina cover layer.

References