



Communication CH₃SH and H₂S Sensing Properties of V₂O₅/WO₃/TiO₂ Gas Sensor

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Abstract: Resistive-type semiconductor-based gas sensors were fabricated for the detection of methyl mercaptan and hydrogen sulfide. To fabricate these sensors, $V_2O_5/WO_3/TiO_2$ (VWT) particles were deposited on interdigitated Pt electrodes. The vanadium oxide content of the utilized VWT was 1.5, 3, or 10 wt.%. The structural properties of the VWT particles were investigated by X-ray diffraction and scanning electron microscopy analyses. The resistance of the VWT gas sensor decreased with increasing methyl mercaptan and hydrogen sulfide gas concentrations in the range of 50 to 500 ppb. The VWT gas sensor with 3 wt.% vanadium oxide showed high methyl mercaptan and hydrogen sulfide responses and good gas selectivity against hydrogen at 300 °C.

Keywords: gas sensor; vanadia-tungsten-titania; semiconductor; methyl mercaptan; hydrogen sulfide



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1. Introduction

Human breath contains small amounts of biomarker gases, such as hydrogen (H₂), nitric oxide (NO), carbon monoxide (CO), methane (CH₄), and various volatile organic components, at low concentrations ranging from several parts per billion (ppb) to parts per million (ppm) [1–4]. The organoleptic intensity of oral malodor correlates with the levels of methyl mercaptan (CH₃SH) and hydrogen sulfide (H₂S), which are volatile sulfur compounds, in human breath [4]. Although monitoring CH₃SH and H₂S concentrations in human breath is one of the best noninvasive screening tests for early diagnosis, the screening process requires an analytical device with sufficient accuracy at the ppb level. The concentration level of H₂ in human breath has been measured to be several tens of ppm, which is higher than those of the other gases [5].

Semiconductor-based gas sensors are effective for respiratory gas analysis from the standpoints of cost, compactness, and power consumption [6–11]. Su et al. reported that for NO₂ sensing, a wearable, alveolus-inspired active membrane sensor based on the WO₃ system showed excellent selectivity and thermal and humidity stability [6]. Jha et al. prepared chemiresistive sensors using MoSe₂ nanoflakes for ppb-level H₂S gas detection [7]. Li et al. synthesized CuO nanosheets by a hydrothermal method and used them to fabricate a sensor, which showed ppb-level H₂S gas response [8].

Our group has reported a resistive-type SO₂ gas sensor based on $V_2O_5/WO_3/TiO_2$ (VWT) [12,13]. Although this gas sensor has been confirmed to respond well to 20 to 5000 ppm SO₂ gas, its responsiveness to methyl mercaptan and hydrogen sulfide has not been investigated. In this study, VWT-based gas sensors with V_2O_5 contents of 1.5, 3.0, and 10 wt.% were prepared. The responsiveness of the gas sensor to ppb-level methyl mercaptan and hydrogen sulfide was investigated. To discuss the gas selectivity of the gas sensor, the sensor response to H_2 gas at the ppm level was investigated.

2. Materials and Methods

After stirring 10 g of TiO₂ nanoparticles (Evonik Aeroxide P 25) in 115 mL of ionexchanged water, 0.444 g of ammonium vanadate (FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan), 1.27 g of ammonium paratungstate (Sigma-Aldrich, St. Louis, MO, USA), and 12 mL of 4% methylamine aqueous solution were added. After mixing for 24 h, the solution was dried at 85 °C to obtain a dry sample. The dry sample was ground and calcined at 450 °C for 5 h to obtain $3V_2O_5/10WO_3/87TiO_2$ (wt.%) (3 VWT) particles. $1.5V_2O_5/10WO_3/88.5TiO_2$ (1.5 VWT) and $10V_2O_5/10WO_3/80TiO_2$ (10 VWT) particles were prepared in the same manner.

The sample powders were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses. XRD analysis was carried out using a SmartLab X-ray diffractometer (Rigaku Corporation, Tokyo, Japan) equipped with a copper source (Cu K α) and one-dimensional high-speed detector (D/teX Ultra 250). The X-ray generator was operated at 40 kV and 30 mA. SEM analysis was performed using a JSM-6335FM microscope (JEOL Ltd., Tokyo, Japan) equipped with a field-emission gun. To obtain the Brunauer–Emmett–Teller (BET) surface areas, the nitrogen adsorption isotherms of sample particles (degassed at 300 °C for 2 h) were measured at 77 K in liquid nitrogen using a NOVA 4200e surface area and pore size analyzer (Quantachrome Instruments, Boynton Beach, FL, USA).

A ceramic paste of VWT particles was prepared by mixing an organic vehicle consisting of 10 wt.% ethyl cellulose and 90 wt.% terpineol. The mixing weight ratio of VWT and the organic vehicle was 2:1.33. The paste was screen-printed onto an alumina substrate with Pt interdigital electrodes with line and space definitions of 100 μ m each. These sensor elements were baked at 750 °C for 20 min to prepare a gas sensor with a sensing film having a thickness of approximately 5 μ m. Figure 1 shows a schematic illustration of the sensor.



Figure 1. Schematic illustration of the $V_2O_5/WO_3/TiO_2$ (VWT) sensor.

The gas responsiveness of the sensor was examined using a test chamber in an electric furnace at 300–500 °C. After placing the sensor in the chamber, dry air was flowed into the chamber for 1 h, followed by the sample gas in dry air for 1 h, at a flow rate of 200 mL/min. The CH₃SH and H₂S gas concentrations were controlled to 0, 50, 250, and 500 ppb in dry air. Sensor resistances in various gas atmospheres were measured by the two-terminal method with a K2700 digital multimeter (Keithley) at 5 s intervals. The response value (*S*) was defined by the following equation: $S = R_a/R_g$, where R_a denotes the resistance in dry air before sample gas exposure and R_g is the resistance after 1 h of sample gas exposure.

The response of the sensors to H_2 gas was investigated using the same apparatus as that used to measure the CH_3SH and H_2S gas responses. The H_2 gas concentration was controlled to 0, 250, and 500 ppm in dry air.

3. Results and Discussion

Figure 2 shows the XRD patterns of the 1.5 VWT, 3 VWT, and 10 VWT particles. Peaks of TiO₂ (anatase and rutile) and WO₃ were observed in all XRD patterns. In addition, peaks of V₂O₅ were confirmed in the 10 VWT XRD pattern. No V₂O₅ peaks were observed in the XRD patterns of 1.5 VWT and 3 VWT owing to the lower V₂O₅ content. Since the peaks assigned to TiO₂, WO₃, and V₂O₅ were observed, no structural changes due to the formation of the complex oxide of V-W-Ti-O were observed.



Figure 2. XRD patterns of 1.5 VWT, 3 VWT, and 10 VWT particles.

Figure 3 shows the SEM images of the 1.5 VWT, 3 VWT, and 10 VWT particles. For all samples, uniform particles with diameters of several tens of nanometers were confirmed. As these diameters are almost the same as those of TiO₂ particles (P 25), it is assumed that V_2O_5 and WO_3 are supported on the surface of the TiO₂ particles in VWT. The BET surface areas of the 1.5 VWT, 3 VWT, and 10 VWT particles were 46, 47, and 34 m²/g, respectively. When compared, 10 VWT had a slightly lower BET surface area than 1.5 VWT and 3 VWT. Since the specific surface area of P 25 TiO₂ is 57.4 m²/g [14], decreasing the amount of TiO₂ decreased the BET surface area of VWT. Although the difference in particle morphology could not be confirmed in Figure 3, the difference in the specific surface area may be due to the difference in particle morphology.

Figure 4 shows the Arrhenius plots of R_a for the 1.5 VWT, 3 VWT, and 10 VWT gas sensors. R_a decreased with decreasing TiO₂ content in VWT. R_a changed exponentially with the reciprocal of temperature between 300 and 500 °C, as shown in the following equation: $R_a = R_0 \exp(-E/RT)$, where *E* is the activation energy, *T* is the temperature in Kelvin, *R* is the gas constant, and R_0 is the pre-exponential factor. This indicates that there is no change in the mechanism of electron conduction in VWT between 300 and 500 °C. The activation energies for electron conduction in the 1.5 VWT, 3 VWT, and 10 VWT gas sensors were 0.57, 0.40, and 0.34 eV, respectively. It is considered that the sensor resistance decreased owing to the decrease in the TiO₂ content in VWT, resulting in a decrease in the activation energy.



Figure 3. SEM photographs of (a) 1.5 VWT, (b) 3 VWT, and (c) 10 VWT particles.



Figure 4. Arrhenius plots of the resistance in dry air (*R*_a) of the 1.5 VWT, 3 VWT, and 10 VWT gas sensors.

Figure 5 shows the CH₃SH gas (50, 250, and 500 ppb) response characteristics of the 1.5 VWT, 3 VWT, and 10 VWT gas sensors at 300 °C. The resistance of all sensors began to decrease with CH₃SH exposure. This is the response of a typical *n*-type semiconductor gas sensor. All gas sensors showed a clear response, even at 50 ppb CH₃SH. The resistance of



all sensors decreased with increasing CH_3SH gas concentration. The response of the *n*-type semiconductor gas sensor to H_2S gas was similar.

Figure 5. CH₃SH gas (50, 250, and 500 ppb) response characteristics of the (**a**) 1.5 VWT, (**b**) 3 VWT, and (**c**) 10 VWT gas sensors at 300 °C.

Figure 6 shows the relationship between the response value to 500 ppb CH₃SH and 500 ppb H₂S and operating temperature. High CH₃SH response values (S = 1.74, 1.74, and 1.33) were obtained for the 1.5 VWT, 3 VWT, and 10 VWT gas sensors at 400, 300, and 300 °C, respectively. In addition, high H₂S response values (S = 1.29, 1.44, and 1.13) were obtained for the 1.5 VWT, 3 VWT, and 10 VWT gas sensors at 400, 400, and 300 °C, respectively. The response to CH₃SH was higher than that to H₂S. The reaction mechanism between the CH₃SH and H₂S gases and the oxygen (O₂²⁻) adsorbed on the surface of VWT is expected to be as follows:

$$CH_3SH + 3O_2^{2-} \rightarrow CO_2 + 2H_2O + SO_2 + 6e^-$$
 (1)

$$H_2S + 3/2O_2^{2-} \rightarrow H_2O + SO_2 + 3e^-$$
 (2)



Figure 6. Relationship between the response values (*S*) to (**a**) 500 ppb CH₃SH and (**b**) 500 ppb H₂S and operating temperature. *S* was calculated as the ratio of the resistance in dry air before (R_a) and after (R_g) sample gas exposure.

Equation (1) shows that 1 mol of CH_3SH reacts with the adsorbed oxygen to form 6 mol of conduction electrons (e⁻). Equation (2) shows that 1 mol of H_2S reacts with the adsorbed oxygen to form 3 mol of e⁻. The generated e⁻ moves to VWT and reduces the sensor resistance. Therefore, if the reaction rates of CH_3SH and H_2S with the adsorbed oxygen are almost the same, it is considered that the response to CH_3SH is higher than that

to H_2S . The 10 VWT gas sensor showed smaller response values to the CH_3SH and H_2S gases. As V_2O_5 oxidizes SO_2 to SO_3 , it is thought that the oxidation of the SO_2 generated from CH_3SH and H_2S leads to a decreased sensor response [15].

Figure 7 shows the relationship between the response value and CH₃SH, H₂S, and H₂ gas concentrations at 300 and 400 °C. At 300 °C, the CH₃SH response value of the 3 VWT gas sensor was large. At 400 °C, the CH₃SH response value of the 1.5 VWT gas sensor was also large. The 1.5 VWT gas sensor showed a slight response to H₂ gas with S = 1.1-1.22. On the other hand, the 3 VWT and 10 VWT gas sensors showed no response to H₂ gas with S = 1.00 and S = 1.02, respectively. Since the H₂ gas response decreased with increasing V₂O₅ content in VWT, V₂O₅ seems to suppress the response to H₂ gas. We will investigate the mechanism of suppressing the H₂ gas response by V₂O₅ in the future.



Figure 7. Relationship between the response value *S* and CH₃SH, H₂S, and H₂ gas concentrations at (a) 300 and (b) 400 °C. *S* was calculated as the ratio of the resistance in dry air before (R_a) and after (R_g) sample gas exposure.

It was found that at 300 °C, the 3 VWT gas sensor had good gas selectivity against H_2 gas and a high CH_3SH response of 500 ppb (S = 1.74). This CH_3SH response value is smaller than that of the WO₃ gas sensor in earlier reports [10,11]. In this study, the H_2S , CH_3SH , and H_2 gas response characteristics in dry atmosphere were measured only once. The long-term stability, reproducibility, and influence of humidity will be investigated in a future study. Although it is necessary to improve the CH_3SH response value, it is considered that the 3 VWT gas sensor has a high potential as a gas sensor for the detection of halitosis because it has excellent gas selectivity against H_2 gas.

4. Conclusions

In this study, CH_3SH and H_2S gas sensors using VWT as a sensitive film were prepared, and their sensing characteristics were investigated. The synthesized VWT particles had a diameter of several tens of nanometers, and no V-W-Ti-O composite oxide was formed. The CH_3SH response value of the VWT gas sensor was higher than the H_2S response value. The 3 VWT gas sensor showed high CH_3SH and H_2S gas responses and good gas selectivity against H_2 gas.

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