**Effect of Oxide-Electrode Interface on Dilute NO₂ Sensing Properties of WO₃ Thin Film Nanosensors**

Jun TAMAKI, a,⁎ Yu OKOCHI, a and Satoshi KONISHI

a Department of Applied Chemistry, Faculty of Science and Engineering, Ritsumeikan University (1-1-1 Noji-higashi, Kusatsu-shi, Shiga 525-8577, Japan)
b Department of Micro System Technology, Faculty of Science and Engineering, Ritsumeikan University (1-1-1 Noji-higashi, Kusatsu-shi, Shiga 525-8577, Japan)

Received August 31, 2005 : Accepted November 4, 2005

The WO₃ thin film nanosensors have been fabricated by dropping and calcination of H₂WO₄ suspension onto Au nano-gap electrode (100 nm of gap-size and 10 μm in width), which was fabricated by means of MEMS (Micro Electro-Mechanical Systems) techniques, photolithography and FIB. The amount of WO₃-electrode interface was controlled by changing amount of WO₃ grains packed in the nano-gap electrode. The sensitivity to dilute NO₂ was increased with increasing amount of interface, suggesting the importance of oxide-electrode interface in NO₂ sensing. Further, the response behavior was affected by the amount of WO₃ grains packed in nano-gap electrode.

**Key Words :** WO₃ Gas Sensor, Dilute NO₂ Sensing, Nano-gap Electrode, Oxide-electrode Interface

1 Introduction

High sensitivity gas sensors are increasingly demanded in the fields of environmental monitoring, VOCs (Volatile Organic Compounds) monitoring in house and car, welfare, and medical applications.1)−3) Semiconductor gas sensors, which can detect dilute gases from the resistance change of oxide semiconductor, are strong candidate for such purposes because of their high sensitivity, simple structure, compact size, low cost and so on. The WO₃ sensors for the detection of NO₂ have been actively investigated aiming at environmental monitoring. Namely, the WO₃ sensors have been sensitized by adopting thin film structure,4)−6) doping foreign oxides,7)−8) and using lamella-type WO₃ particles.9)−10) Recently, the authors focused the electrode structure, i.e., the gap-size of electrode. Since the size of oxide grain is several tens−several hundreds nm, it is very interesting what happens when the gap-size is decreased comparable to size of oxide grain. Under this concept, the effect of gap-size on sensing properties to dilute NO₂ has been investigated for WO₃ nanosensors equipped with nano-gap electrode, which were fabricated by means of MEMS techniques.11) The sensitivity to dilute NO₂ was increased with decreasing gap-size when the gap-size was decreased less than 0.8 μm. When the gap-size was decreased, the number of oxide grains and thus that of grain boundaries were decreased. The increasing sensitivity was attributed to the increasing contribution of oxide-electrode interface. The sensitivity at interface was much higher than that at grain boundary, inducing the increase in sensitivity when the gap-size was decreased. The similar phenomena were also observed for dilute Cl₂ sensing using In₂O₃ thin film nanosensors.12) It was concluded that the importance of oxide-electrode interface was demonstrated with nanosensor and that nano-design of electrode structure resulted in the high sensitivity gas sensors.

In this study, the effect of WO₃ grain packing at nano-gap electrode on NO₂ sensing properties was investigated in order to elucidate the effect of oxide-electrode interface. Namely, the number of WO₃ grains was changed at nano-gap electrode and thus the amount of interface was controlled. The relationship between the amount of interface and the NO₂ sensitivity was investigated.

2 Experimental

The nano-gap electrode was fabricated on SiO₂/Si substrate by means of MEMS techniques (photolithography and FIB). First, the Au line of 10 μm in width and 300 nm in thickness was designed on SiO₂/Si substrate by conventional photolithography (lift-off method). Second, the Au line was etched by FIB (focused ion beam technique, Hitachi FB-2100) using Ga⁺ ion beam. The etching width was set to 100 nm and thus the nano-gap electrode with 100 nm gap-size and 10 μm line width was obtained.

The suspension was prepared by mixing H₂WO₄ and ethylene glycol. The microdrop of H₂WO₄ suspension was dropped onto Au nano-gap electrode by using micromanipulator (Eppendorf, InjectMan N12 and FemtoJet), dried and calcined at 400 °C in air for 3h, to be WO₃ thin film nanosensor. The thickness of film was controlled to be visible the electrode gap and to vary the number of WO₃ grains included in the nano-gap. The schematic drawing of WO₃ thin film nanosensor used in this study is shown in Fig. 1. The surface morphology of WO₃ thin film nanosensor was observed by means of SEM (Hitachi, S-4800).

The sensing properties to dilute NO₂ were examined with the flow apparatus at 200 °C. The NO₂ concentra-
tion was varied in the range of 0.01-1 ppm. The gas sensitivity (S) was defined as the ratio (S=Rg/Ra) of sensor resistance in NO₂ containing air (Rg) to that in air (Ra).

3 Results and Discussion

The number of WO₃ grains was controlled by changing the amount of microdrop of H₂WO₃ suspension. Figure 2 shows the SEM images of nano-gap electrode for WO₃ thin film nanosensors. The sensors were denoted as Sensor 1, 2, and 3 in the order of Fig. 2-(a), (b), and (c), respectively. For Sensor 1, the nano-gap electrode was clearly observed to be 100 nm of gap-size and 10 μm in width. The WO₃ grains were partly included in the nano-gap electrode. The number of WO₃ grains included in the gap was increased with going from Sensor 1 to Sensor 2 and 3, although WO₃ grains were not packed in the whole width of nano-gap electrode in all of these sensors. Since the WO₃-electrode interface is formed at the part where WO₃ grains are packed, it is considered that the amount of WO₃-electrode interface is increased with going to Sensor 1, 2, and 3. The gap-size is very small (100 nm) and thus it is considered that the contribution of interface increase is large when WO₃ grain packing is increased.

By using these sensors, the effect of oxide-electrode interface on NO₂ sensing properties was investigated. In order to evaluate the amount of interface, it was measured how long the WO₃ grains were packed in the 10 μm electrode width. This was defined as the packing length and estimated as 2.7, 4.6, and 7.1 μm for Sensor 1, 2, and 3, respectively. The larger packing length means the greater amount of WO₃-electrode interface. Figure 3 depicts the sensitivities to dilute NO₂ of various WO₃ thin film nanosensors at 200 °C as a function of packing length. In the whole concentration range (0.05-0.5 ppm), the sensitivity was increased with increasing packing length. This suggests that the higher sensitivity is obtained with the nanosensor having the greater amount of interface. As demonstrated in Refs. 11 and 12, the importance of oxide-electrode interface was again recognized here. It was observed from Fig. 2 that the WO₃ grains were also deposited at the part other than nano-gap. Since the sensor resistance was determined with the WO₃ grains in nano-gap and the measurement of sensing properties was performed in flow apparatus, the WO₃ grains other than nano-gap are not considered to influence the sensor resistance.

Figure 4 shows the response transients of WO₃ thin film nanosensors (Sensor 1 to 3) to 0.5 ppm NO₂ at 200 °C. The output voltage was decreased upon exposure to NO₂ for all sensors, indicating the response of resistance increase. Since NO₂ is the oxidizing gas, NO₂ molecule is negatively adsorbed on the WO₃ surface as shown in equation 1.

\[
\text{NO}_2 + e^- \rightarrow \text{NO}_2^{-\text{ads}}
\]  

![Fig. 1 Schematic drawing of WO₃ thin film nanosensor equipped with nano-gap electrode.](image)

![Fig. 2 SEM images of the nano-gap electrode (10 μm in width) for WO₃ thin film nanosensors. The number of WO₃ grains packed at the nano-gap was increased in the order of Sensors 1, 2, and 3.](image)
WO$_3$ is n-type semiconductor and thus the resistance of WO$_3$ nanosensor is increased due to the adsorption of NO$_2$.

The output voltage for Sensor 1 was somewhat noisy compared with other sensors. The packing of WO$_3$ grains was the least for Sensor 1 and thus the WO$_3$ grains might be easy to move in the nano-gap electrode, causing the noise. Further, the response behavior was influenced by the packing of WO$_3$ grains. The output voltage was gradually decreased after sudden decrease upon exposure to NO$_2$ for Sensor 1. However, this gradual decrease was diminished with increasing number of WO$_3$ grains packed at the nano-gap. The diffusions of NO$_2$ as well as O$_2$ are considered to be related to NO$_2$ sensing of WO$_3$ sensor as proposed in Ref. 13.

4 Conclusions

The effect of WO$_3$-electrode interface on NO$_2$ sensing properties is evaluated for WO$_3$ thin film nanosensors with Au nano-gap electrode (100 nm of gap-size and 10 μm in width). The sensitivity to dilute NO$_2$ is increased with increasing amount of interface, suggesting the importance of oxide-electrode interface in gas sensing of semiconductor gas sensors. Further, the response behavior is affected by the amount of WO$_3$ grains included in nano-gap electrode. The larger amount of packed WO$_3$ grains brings about the faster rate of response.

Acknowledgment

A part of this research was performed within Grant-in-Aid for Scientific Research and the 21 century COE program “Micro/Nano Science and Integrated Systems” supported by the Ministry of Education, Science, Sports and Culture, Japan.

References

4) J. Tamaki, A. Hayashi, Y. Yamamoto, and M.