Sensors and Materials, Vol. 24, No. 1 (2012) 13–19
MYU Tokyo

S & M 0865

Effect of High-Humidity Aging on Performance of Tungsten Oxide-Type Aromatic Compound Sensors

Toshio Itoh*, Ichiro Matsubara, Jun Tamaki[1], Kenji Kanematsu[1], Woosuck Shin, Noriya Izu and Maiko Nishibori

National Institute of Advanced Industrial Science and Technology (AIST),
Shimo-Shidami, Moriyama-ku, Nagoya 463-8560
[1]Department of Applied Chemistry, Faculty of Science and Engineering,
Ritsumeikan University, Kusatsu, Shiga 525-8577

(Received January 24, 2011; accepted February 28, 2011)

Key words: tungsten oxide, aromatic compound, toluene, high-humidity aging

WO_3-type toluene gas sensors have been shown to be affected by humidity. The high-humidity aging effect is investigated on these sensors. High-humidity aging treatment is found to be effective against the effects of humidity on WO_3-type toluene sensors. This humidity independence can be explained in the terms of a change in the surface conditions of WO_3 grains.

1. Introduction

The sick building syndrome is caused by harmful volatile organic compounds (VOCs) even if the concentration of the VOCs is at the ppb level. Aromatic compounds are widely known to be an important cause of the sick building syndrome. A number of studies on developing high-sensitivity aromatic compound sensors have been carried out.[1–5] The Ministry of Health, Labour and Welfare of Japan stipulates that the concentration of toluene in indoor room air should be less than 70 ppb.[6] It is therefore desirable to use a series of high-sensitivity VOC sensors such as aromatic compound sensors.

Metal oxides are some of the best materials for use as VOC sensors for a simple gas sensor system. We previously reported on high-sensitivity WO_3-type gas sensors for aromatic compounds.[7] The selective sensing properties of WO_3-type gas sensors

*Corresponding author: e-mail: itoh-toshio@aist.go.jp

can be controlled on the basis of temperature. They show good response to NO_2 and aromatic compounds at low (approximately 200°C) and high (approximately 400°C) temperatures, respectively.[7–12] It has been reported that the gas-sensing response of 700°C-annealed WO_3 is not affected by humidity for ppm-level NO_2 detection at low temperatures.[13] However, humidity has an effect on WO_3 in cases of H_2S[13] and aromatic compound detection, i.e., combustion mechanism. The sensor response of WO_3 to aromatic compound gases is decreased in high-humidity atmospheres. This problem needs to be resolved in order to realize the operation of WO_3-type gas sensors under ambient conditions. We have reported that high-humidity aging improves the immunity to humidity of the sensor responses of Pt, Pd, and Au/SnO_2 systems in the case of combustion gas sensing.[14] In this study, we investigated improvements in the stability of the gas-sensing properties of WO_3 under various humidity conditions.

2. Materials and Methods

2.1 *Synthesis of WO_3 films as aromatic sensors*

The synthesis of WO_3 films for use as gas sensors was carried out using the method described in our previous report.[7–12] An aqueous solution of $(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$ was neutralized by a dilute nitric acid solution yielding H_2WO_4 precipitate. The precipitate was thoroughly washed with deionized water, dried, and then dispersed into ethylene glycol forming a suspension. A microdrop of the suspension was dropped on a 175×175 μm^2 area of a silicon substrate with a platinum heater and platinum comb-type electrodes, with a gap of 2 μm, using a micromanipulator. This was then dried and calcined at 400°C for 3 h. The resulting WO_3 film consisted of densely packed disk-shaped particles of submicron diameters.[7–12]

2.2 *High-humidity aging*

High-humidity aging of the WO_3 films was carried out in pure air with a relative humidity (RH) up to 90% at room temperature. The humid air had a flow rate of 250 mL/min. The elements were heated to 500°C and maintained at this temperature for approximately 2 weeks using a Pt heater.

2.3 *Gas sensing properties*

The gas sensing properties of the WO_3 films were experimentally determined using a flow apparatus. Synthetic air (Japan Fine Products "G1" grade) was flowed into a water bubbler. The RH of the synthetic air was set at 25, 50, and 75% at 20°C by controlling the temperature of the water bubbler. The films were heated to 400°C using the Pt heater. Toluene vapor was generated using a Gastec PD-1B gas permeator. The concentration of the toluene gas was controlled to below 70 ppb. The total flow was always 200 mL/min. The sensor response is defined using eq. (1),

$$S = \frac{R_a}{R_g}, \tag{1}$$

where S, R_a, and R_g denote the sensor response magnitude, resistance in pure humid artificial air, and resistance in toluene gas with humid artificial air, respectively.

3. Results and Discussion

3.1 *Sensing properties of the WO_3*

The dynamic normalized resistance responses of the WO_3 films before high-humidity aging for 70 ppb toluene gas at 400°C for humidity values of 25, 50, and 75%RH are shown in Fig. 1. All the resistance profiles are normalized at the initial change in gas flow from pure air to air with toluene vapor. It is seen that the WO_3 films exhibit distinct responses to toluene vapor. A decrease in resistance of WO_3 occurs when toluene vapor combustion takes place on the surface of the WO_3 grains. Oxygen molecules from the ambient atmosphere are adsorbed onto the surfaces of the WO_3 grains and form an electron depletion layer. During exposure to toluene gas, the electron depletion layer is reduced since the combustion of toluene gas consumes the adsorbed oxygen molecules.[15–17] The resistance of the WO_3 films decreased with increasing toluene concentration, and almost reached saturation in at least 1 min. The resistance of the nonaged WO_3 films caused by 70 ppb toluene gas decreased when the humidity was increased. Thus, the sensor response of the WO_3 films depends on humidity, and it was confirmed that the combustion effect of WO_3 is disturbed by moisture.

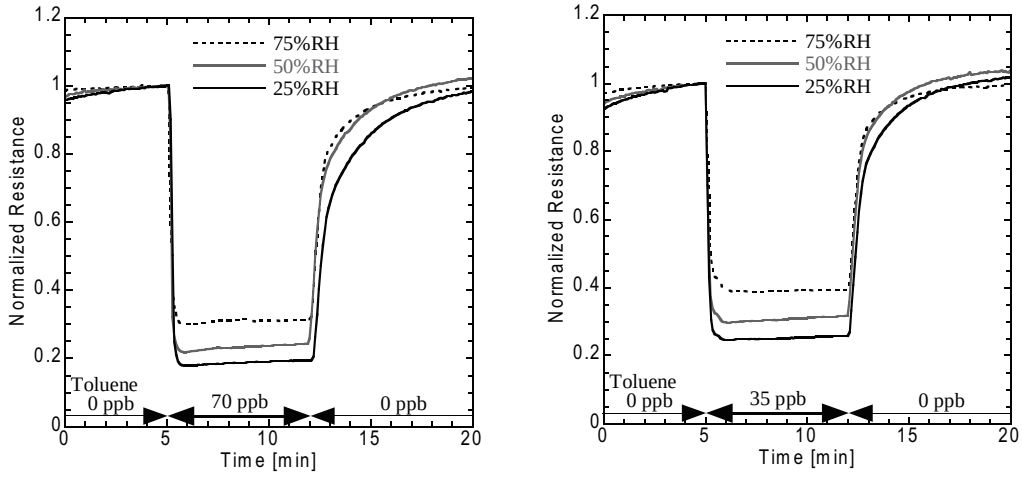

Fig. 1. Normalized resistance profiles of nonaged WO_3 films in humid artificial air with and without toluene gas. Toluene concentrations are (a) 70 ppb and (b) 35 ppb. The normalization of resistance is based on the resistance at 5 min.

Figure 2 shows the dynamic resistance response of the WO_3 films after high-humidity aging. A series of resistance measurements of the aging-treated WO_3 also show distinct responses to toluene gas. For the aging-treated WO_3, the decrease in resistance caused by the toluene gas does not change much when the humidity was increased. All the profiles in Fig. 2 are almost identical. Thus, the sensor response of the aging-treated WO_3 is independent of humidity.

The sensor response (S) of the WO_3 films to 35 and 70 ppb toluene gas under different humidity conditions is summarized in Fig. 3. The plots show that the sensor response of the nonaged WO_3 films depends significantly on humidity. The sensor response to 70 ppb toluene gas under 75%RH is smaller than the sensor response to half the concentration, i.e., 35 ppb toluene gas, under 25%RH. The nonaged WO_3 film cannot be used to monitor the exact toluene concentrations within the levels that cause the sick building syndrome. The aging-treated WO_3 film shows good gas sensing performance because the sensor response to 35 and 70 ppb toluene gas barely changes even when the humidity changes. Consequently, these results prove that high-humidity aging treatment is effective for achieving independence from humidity effects for the WO_3-type toluene sensor.

3.2 *High-humidity aging effects*

The high-humidity aging treatment is also effective for the resistance increase of WO_3 in pure air. In the case of 75%RH, the resistances of the nonaged and aging-treated WO_3

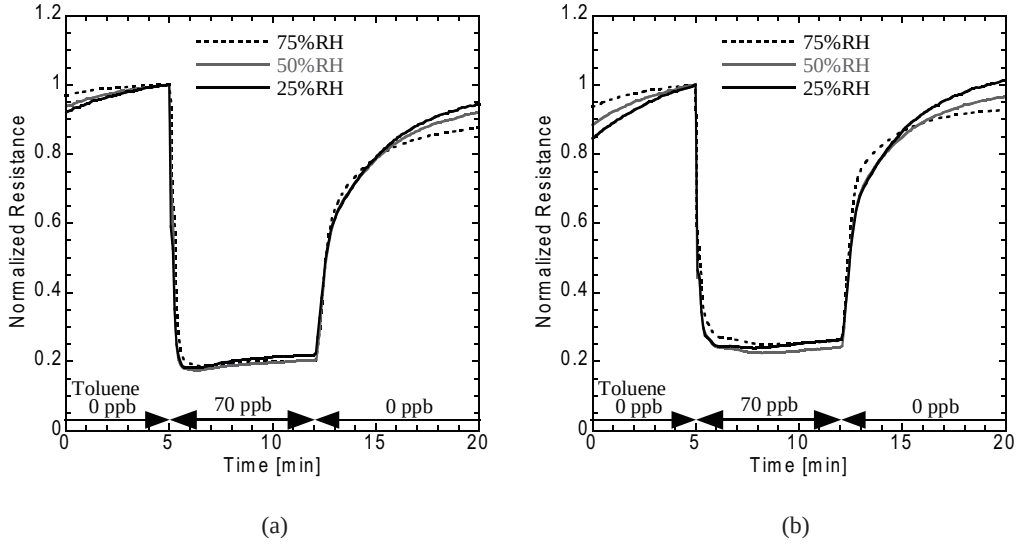

Fig. 2. Normalized resistance profiles of WO_3 films after high-humidity aging in humid artificial air with and without toluene gas. Toluene concentrations are (a) 70 ppb and (b) 35 ppb. The normalization of resistance is based on the resistance at 5 min.

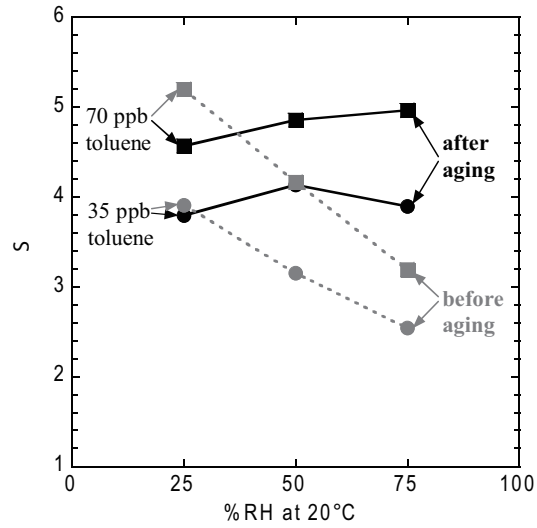

Fig. 3. Sensor response (*S*) of the WO_3 films to toluene gas at concentrations of 35 and 70 ppb under different humidity conditions.

at the initial change in gas flow from pure air to air with toluene vapor are 486 kΩ and 1.68 MΩ, respectively. It is indicated that the high-humidity aging treatment promotes the oxidation to WO_3, i.e., decreasing carrier electrons into WO_3. It is therefore considered that the sensor responses of the WO_3 films are mostly improved by the high-humidity aging treatment, as shown in Fig. 3.

Jimenez *et al*. have reported the humidity dependence of the response of WO_3 with its structural defects.[13] The surface morphology of WO_3 depends on the annealing temperature. The WO_3 annealed at 400°C has structural defects, which correspond to oxygen deficiency. The amount of structural defects is decreased with the increase in annealing temperature (from 400 to 700°C, for 5 h). In this report, the responses of WO_3 to hydrogen sulfide are almost equal under more than 50%RH conditions, and WO_3 under low- or no-humidity condition shows higher response than that under more than 50%RH condition. Therefore, the oxidation of WO_3 is insufficient for the humidity independence of the sensor responses.

In the case of the high-humidity aging, the responses of WO_3 to the combustion gas, toluene, are almost equal in the range of 25–75%RH. Therefore, the humidity dependence is affected by the high-humidity aging effect as well as the structural effect. We propose a high-humidity aging mechanism to improve the gas-sensing properties of WO_3. This humidity independence effect can be explained by the change in the surface conditions of the WO_3 grains. Figure 4 shows the surface of the WO_3 grains under

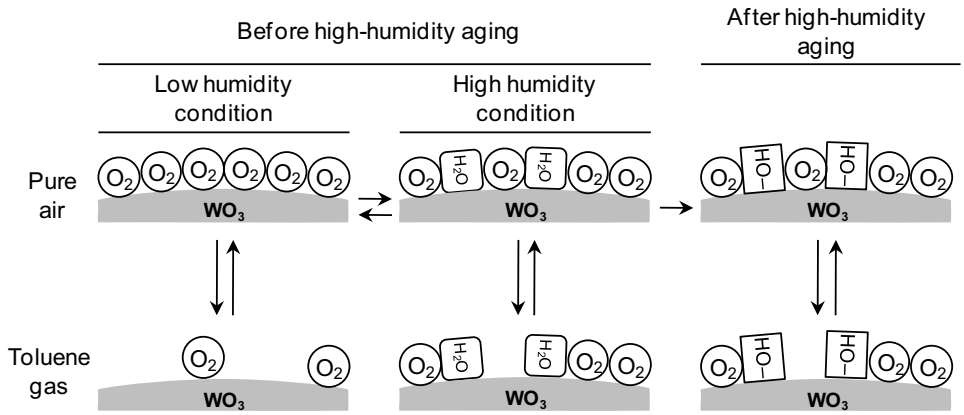

Fig. 4. Surface of the WO_3 grains under several conditions.

different conditions. In the case of the nonaged WO_3, under a high-humidity condition, the sensor response to toluene is decreased compared with that under the low-humidity condition, since the adsorbed water competes with oxygen at water-adsorbable sites. Therefore, the humidity change affects toluene combustion, i.e., the sensor response, for the WO_3 sensor. On the other hand, heat treatment of WO_3 under a high-moisture condition promotes the adsorption of water molecules, which bind to the WO_3 framework as hydroxyl groups, and the water-adsorbable sites are therefore blocked. Since the amount of water adsorbed is not changed under different humidity conditions, the sensor response of the aging-treated WO_3 is stable.

We have reported that the high-humidity aging treatment is also effective for palladium-loaded SnO_2, but not effective for the non-palladium-loaded SnO_2.[14] It is considered that palladium plays an important role in the formation of hydroxyl groups on the surface of SnO_2.[14] However, the high-humidity aging treatment is effective for pristine WO_3, that is, non-palladium-loaded WO_3. The surface condition of WO_3 seems to be different from that of SnO_2, although the reasons are not completely elucidated; the conditions should be studied in the future.

4. Conclusions

The sensor response of the nonaged WO_3 depends on humidity conditions. The high-humidity aging improves the humidity independence of the sensor responses of the WO_3 systems to toluene gas. The aging-treated WO_3 film shows responses to the toluene gas, which are independent of humidity from 25 to 75%RH. We propose a mechanism for the effects of the high-humidity aging on the basis of this phenomenon.

Acknowledgements

We express our sincere thanks to Professor Kengo Shimanoe of Kyushu University for his advice. Thanks are also extended to Panasonic Electric Works Co., Ltd. for providing the platinum electrode and heater-prepared substrates. This work was supported by the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

References

1 K. Kanda and T. Maekawa: Sens. Actuators, B **108** (2005) 97.
2 S. Ashraf, C. S. Blackman, R. G. Palgrave, S. C. Naisbitt and I. P. Parkin: J. Mater. Chem. **17** (2007) 3708.
3 M.-T. Ke, M.-T. Lee, C.-Y. Lee and L.-M. Fu: Sensors **9** (2009) 2895.
4 T. Kida, T. Doi and K. Shimanoe: Chem. Mater. **22** (2010) 2662.
5 Q. Qia, T. Zhanga, L. Liua and X. Zheng: Sens. Actuators, B **137** (2009) 471.
6 The Ministry of Health, Labour and Welfare web site, http://www1.mhlw.go.jp/houdou/1212/h1222-1_13.html (accessed on 28 December 2010) (in Japanese).
7 New Energy and Industrial Technology Development Organization (NEDO) web site, http://www.tech.nedo.go.jp/PDF/100010386.pdf (accessed on 28 December 2010) (in Japanese).
8 J. Tamaki, A. Hayashi, Y. Yamamoto and M. Matsuoka: Sens. Actuators, B **95** (2003) 111.
9 J. Tamaki, A. Hayashi and Y. Yamamoto: J. Ceram. Soc. Jpn. **112** (2004) S546.
10 J. Tamaki, A. Miyaji, J. Makinodan, S. Ogura and S. Konishi: Sens. Actuators, B **108** (2005) 202.
11 J. Tamaki, A. Miyaji, J. Niimi, Y. Nakataya and S. Konishi: IEEJ Trans. Sens. Micromachine **126** (2006) 573.
12 J. Tamaki, T. Hashishin, Y. Unoa, D. V. Dao and S. Sugiyama: Sens. Actuators, B **132** (2008) 234.
13 I. Jimenez, J. Arbiol, G. Dezanneau, A. Cornet and J. R. Morante: Sens. Actuators, B **93** (2003) 475.
14 T. Itoh, I. Matsubara, M. Kadosaki, Y. Sakai, W. Shin, N. Izu and M. Nishibori: Sensors **10** (2010) 6513.
15 N. Yamazoe: Sens. Actuators, B **5** (1991) 7.
16 N. Yamazoe and K. Shimanoe: Sens. Actuators, B **128** (2008) 566.
17 N. Yamazoe and K. Shimanoe: Sens. Actuators, B **138** (2009) 100.