Transactions of the Materials Research Society of Japan 32[3] 673-676 (2007)

Development of Sheet-Type Hydrogen Sensors

K. Takano, A. Inouye*, S. Yamamoto, M. Sugimoto, A. Sugiyama** and M. Yoshikawa
JAEA, Quantum Beam Science Directorate, 1233 Watanuki, Takasaki, Gunma 370-1292, Japan
Fax: 81-27-346-9687, e-mail: takano.katsuyoshi@jaea.go.jp
*School of Engineering, Tohoku Univ., 6-6 Aramaki Aoba-ku, Sendai 980-8579, Japan
** JAEA, Quantum Beam Science Directorate, 8-1 Umemidai, Kizu-cho, Souraku-gun, Kyoto 619-0215, Japan

The deposition of tungsten oxide thin films on the polymer sheets was performed by reactive r.f. sputtering method. It was found that the tungsten oxide thin film changes the color from transparency to deep blue within few minutes to expose 0.1 % hydrogen, such as to be recognized the change by viewing with the naked eye. The tungsten oxide thin films is useful as convenient sheet-type hydrogen sensors for the utilization of hydrogen in fuel cell as a clean energy source.
Key words: Tungsten oxide, Hydrogen, Gasochromic, Sheets, Sensor

1. INTRODUCTION

Recently, the utilization of hydrogen in fuel cells as a clean energy source has been paid much attention. Hydrogen is colorless, odorless, and inflammable as the large flame propagation velocity. The concentration of lower explosive limit (LEL) in hydrogen is 4 vol.% at room temperature in air. Therefore, the technique of secure and high sensitive detection has been required to develop for the production, the storage, the transportation, and the utilization of hydrogen.

Tungsten oxide thin films as gasochromic materials have been studied for the application of optical hydrogen sensors [1-6], using the reversibly change of the color to be exposed with hydrogen gas (gasochromic coloration). The optical sensors and it's systems have more lightweight, smaller size, simpler structure, and less power than the electrical sensors which detect hydrogen leakage with the change of the thermal voltage and are used most at present [7]. But the rate of the coloration is not high enough to satisfy the specification for hydrogen sensors. The optical sensing characteristic is measuring the gasochromic coloration, i.e., the change of optical transmittance of tungsten oxide thin film. The mechanism of the gasochromic coloration is still not fully understood despite the recent studies [8-11]. In our previous report, crystalline tungsten oxide thin films fabricated by reactive r.f. sputtering method exhibited superior gasochromic coloration to amorphous films [6]. However, to fabrication of the crystalline tungsten oxide needs to heat treatment up to 400 °C with expensive heating equipment which resists the oxidation during the reactive r.f. sputtering. The substrates are limited to be durability materials for the high temperature in the fabrication.

In this work, tungsten oxide thin films with a sheet in which soft materials such as cheap polymers are applied to the substrate with sheets are proposed as sheet-type hydrogen sensors. The sheet-type sensors can wind the pipes and the storage tanks with complex shape. The points or locations with hydrogen leakage are recognized by the viewing of the coloration with the naked eye, without using the photo-detectors. The temperature to deposit tungsten oxide thin film on the cheap polymer sheets is required to be low temperature, because the melting point of the polymer sheets is usually low temperature. Therefore, the fabrication of the sheet-type sensors, are lower the production cost than that of the crystalline tungsten oxide thin films using the heating equipment and heat-resistant materials. To deposit on the polymer sheets at low temperature, the deposition parameters of the tungsten oxide are investigated using reactive r.f. sputtering method. In order to examine the efficiency for the detection of hydrogen leakage, the gasochromic coloration of the tungsten oxide thin film deposited on the polymer sheets is observed with diluted hydrogen.

2. EXPERIMENTAL

The tungsten oxide thin films were prepared by the reactive r.f. magnetron sputtering with a target of W (purity 99.9 %) at room temperature. The deposition chamber equipped with two sputter sources was pumped down to a base pressure of about $5x10^{-4}$ Pa using a turbo-molecular pump. Sputtering gas of purity 99.999 % argon (Ar) and reactive gas of purity 99.99 % oxygen (O_2) were flowed into the deposition chamber through mass-flow meters to obtain the required Ar and O_2 mixture under the pumping condition. The Ar partial pressure was fixed at 150 mPa, and O_2 partial pressure was changed from 18 to 69 mPa. The substrates were selected to be quartz glass (QG) with the thickness of 0.5 mm, Polyvinylchloride (PVC) with the thickness of 11 μm, Polycarbonate (PC) with the thickness of 1.2 mm, Polyethylene (PE) with the thickness of 40 μm, and Polyethylene terephthalate (PET) with the thickness of 100 μm.

The thickness was measured with a surface profiler (DEKTAK3ST, Veeco), and supported by Rutherford backscattering spectroscopy (RBS) analysis. The structure of tungsten oxide films on the QG substrate was characterized by x-ray diffraction (XRD) in which the x-ray source was operated at 40 kV and 30 mA for Cu-$K\alpha$ radiations.

To characterize the gasochromic coloration for hydrogen, a palladium (Pd) which can be used as catalyst material was deposited on the surface of the tungsten oxide thin films using the r.f. sputtering. The thickness of Pd was estimated to be 15 nm. The

gasochromic properties were examined by time resolved optical spectroscopy at room temperature, as described in previous reports [6]. The experimental set up is composed of sealed gas cell to keep concentration of hydrogen, light-emitting diode with the wavelength of 645 nm, and optical spectrometer. The reduction of the transmittance I/I_{air} was measured with an exposure of diluted hydrogen. In this experiment, I_{air} and I are the intensity of light transmitted the film in air and during the hydrogen exposing, respectively. The background of the spectrometer is subtracted from I_{air} and I. In order to investigate the gasochromic coloration of the tungsten oxide thin films with various O_2 partial pressures at deposition, the optical experiments were performed with the concentration of hydrogen at 1 % diluted by Ar gas. For the tungsten oxide film deposited on the PET substrate, the gasochromic coloration with various concentration of hydrogen diluted by nitrogen (N_2) gas was observed on the assumption that the hydrogen sensor with the films is used practically in ambient air.

3. RESULTS AND DISCUSSIONS

3.1 Deposition rate and Structure

For the tungsten oxide thin films deposited on the QG substrate with various O_2 partial pressures, the deposition rate was estimated from the measurement of the thickness and deposition time as shown in Fig. 1. The deposition rate decreased exponentially with the increase the O_2 partial pressure. It is expected that the gasochromic coloration is influenced by the difference of the thickness [12]. To avoid the influencing, the films were made the same thickness, 350 nm, adjusting the deposition time. For example, in the case of the O_2 partial pressure at 22 mPa, the deposition time is adjusted to 30 minutes. On the other hand, the atomic ratio of oxygen atoms to tungsten atoms in the films is expected to be different due to the different O_2 partial pressure [9,10].

The crystallinity of the films was confirmed by XRD. The typical XRD pattern for the films deposited on the QG substrate is shown in Fig. 2(a). The XRD pattern has broad peak at about 22 degrees. The broad peak is considered to the diffraction from amorphous structure

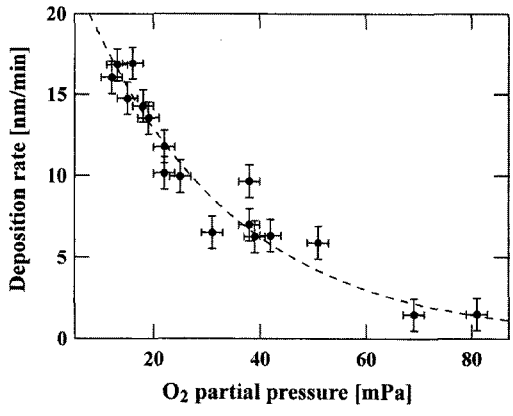

Fig. 1. Deposition rate of the tungsten oxide with various O_2 partial pressures at the reactive r.f. magnetron sputtering. Broken line is a fitting line with an exponential function.

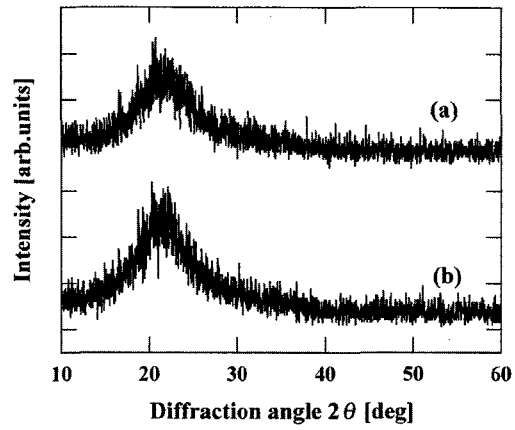

Fig. 2. XRD patterns of tungsten oxide films with the thickness of 350 nm deposited on quartz glass (QG) substrate with the O_2 partial pressure at 22 mPa (a), and QG substrate (b).

of the QG substrate as shown in Fig. 2(b). The films can not be observed crystalline structure. The XRD pattern indicates that the tungsten oxide the films deposited at room temperature have amorphous or microcrystalline structure.

3.2 Gasochromic coloration

The gasochromic coloration of the tungsten oxide thin films deposited on the QG substrate with various O_2 partial pressures was observed, after the deposition of the palladium catalyst. The reduction of the transmittance for the typical films deposited at the different O_2 partial pressures is shown in Fig. 3 as the function of the exposure time. In the case of deposited at 13 mPa, the transmittance decreases gradually during the exposure as shown in Fig. 3(a). The reduction of the transmittance is almost saturated approximately 600 seconds. The saturated value of the transmittance is 0.87. Therefore, the reduction of the transmittance, that is the gasochromic coloration level, is 13 %. In the case of 69

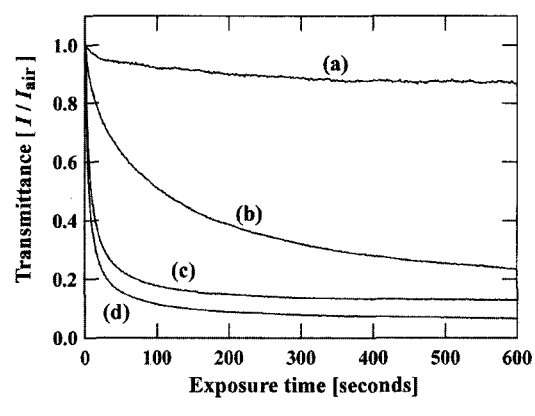

Fig. 3. Gasochromic property of tungsten oxide films with the O_2 partial pressure at 13 mPa (a), 69 mPa (b), 42 mPa (c), and 18 mPa (d), exposed 1% H_2 in Ar.

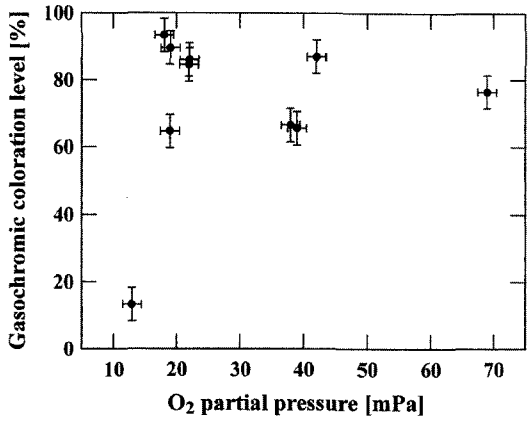

Fig. 4. Gasochromic coloration level for the tungsten oxide thin films deposited on the quartz glass (QG) substrate with various O_2 partial pressures.

mPa, the transmittance gradually decreases as shown in Fig. 3(b). The transmittance is expected to decrease during the exposure of hydrogen more than the exposure time of 600 seconds, but saturate soon. The gasochromic coloration level is assumed to be 77 % at 600 seconds. In the case of 42 mPa, the reduction of the transmittance drastically decreases and saturates to be 0.13 at 600 seconds as shown in Fig. 3(c). The gasochromic coloration level is 87 %. In the case of 18 mPa, the reduction of the transmittance is larger than that of 42 mPa as shown in Fig. 3(d). The gasochromic coloration level is 93 % at 600 seconds.

The gasochromic coloration level of fabricated films is plotted for the O_2 partial pressure as shown in Fig. 4. The gasochromic coloration level has the maximum at 18 mPa, and the minimum at 13 mPa. On the other hand, the gasochromic coloration level is plotted for the deposition rate as shown in Fig. 5. It is found that the gasochromic coloration level has the local maximum at 14 nm/min, and the minimum at 17 nm/min. These distributions of gasochromic coloration level are

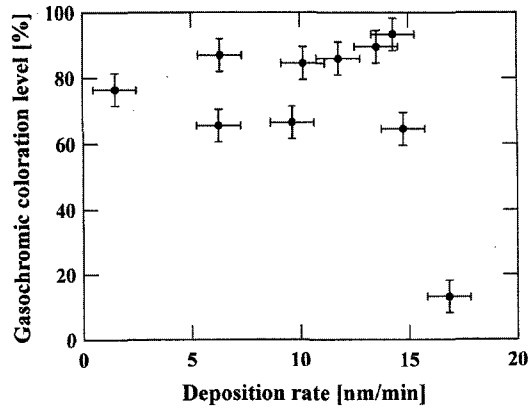

Fig. 5. Gasochromic coloration level for the tungsten oxide thin films deposited on the quartz glass (QG) substrate with various deposition rate.

the tungsten oxide thin film. In the case of the lower supposed to relate to the growth or formation process in deposition rate, the tungsten oxide thin films have higher concentration of oxygen such as full oxidized tungsten, WO_3. In the case of higher deposition rate, the films have lower concentration of oxygen such as sub or non-stoichiometric WO_{3-x} [9,10]. At the deposition rate of 14 nm/min, the defects of oxygen in the tungsten oxide film are considered to be effective in the gasochromic coloration. The tungsten oxide thin films deposited with the deposition rate of 14 nm/min at room temperature have superior gasochromic coloration such as to be expected the application to the hydrogen sensors.

3.3 Efficiency for the detection of hydrogen

The tungsten oxide thin films with the PVC, the PC, the PE, and PET sheet substrate were fabricated by the deposition of tungsten oxide at O_2 partial pressure of 18 mPa, when the deposition rate is 14 nm/min. The reduction of the transmittance for the films was observed with the exposure of 1 % hydrogen, as shown in Fig. 6. The transmittance for all the films decreases to the lower than 0.5 within 20 seconds due to the gasochromic coloration. At the time of 20 seconds, The color of all the films changes from transparency to deep blue such as to be recognized by viewing. In particularly, the gasochromic coloration level of the film deposited on the PET sheet substrate is the largest in all the films, 84 % at 20 seconds.

To investigate a repetitive response for hydrogen, the flowing of 1% hydrogen and stopping of the flow are alternately performed for the tungsten oxide thin film deposited on the PET sheet substrate at several times. The stopping is the similar to be a bleaching with normal ambient air. Figure 7 shows the typical result. The transmittance decreases from 0.7 to 0.3 for 40 seconds blowing the hydrogen, and recovers for 180 seconds. To repeat the blowing and stopping, the decreasing and the recovering reappear similarly. The tungsten oxide thin film can detect the hydrogen, repetitively.

In order to confirm the lower limit of the hydrogen concentration to response, the gasochromic coloration of the tungsten oxide thin film deposited on the PET sheet

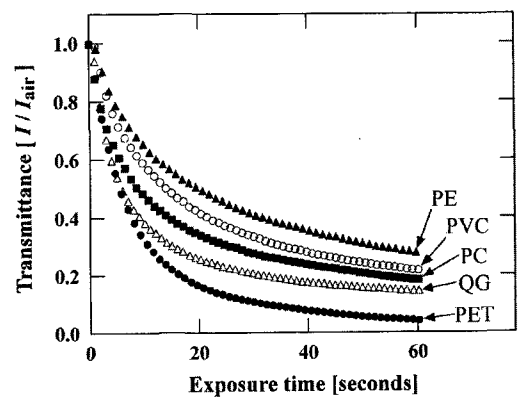

Fig. 6. Gasochromic property for 1% H_2 in Ar of tungsten oxide thin film deposited on the quartz glass (QG), Polyvinylchloride (PVC), Polycarbonate (PC), Polyethylene (PE), and Polyethylene terephthalate (PET).

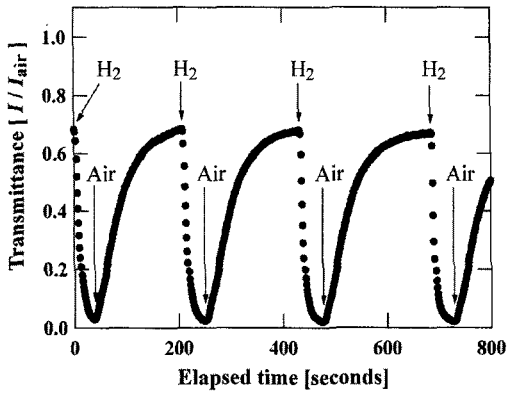

Fig. 7. Repetitive response of tungsten oxide thin film deposited on the PET substrate. The blowing of 1% H_2 and bleaching with normal ambient air are alternately performed at room temperature.

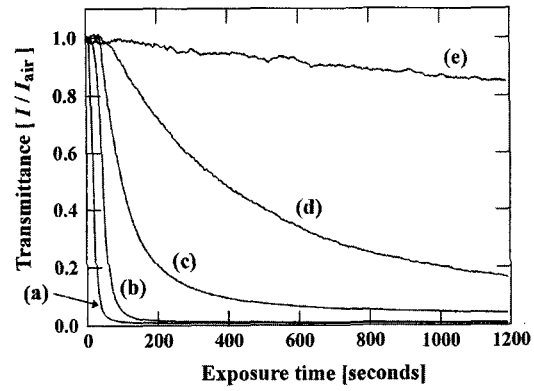

Fig. 8. Response of tungsten oxide thin film deposited on the PET substrate for 1 % (a), 0.5 % (b), 0.1 % (c), 0.05 % (d), and 0.01 % hydrogen (e) diluted by N_2.

substrate was observed with various concentration of hydrogen diluted by N_2. The reduction of the transmittance for the concentration of 1 %, 0.5 %, 0.1 %, 0.05 %, and 0.01 % is shown in Fig. 8(a), 8(b), 8(c), 8(d), and 8(e), respectively. To expose 1 % hydrogen, the transmittance decreases slowly during 6 seconds, and then decreases promptly to be under 0.03 at 60 seconds. With the decrease of the concentration of hydrogen, beginning of the promptly reduction delays, and the rate of the promptly reduction becomes low. In the case of the exposure with 0.01 % hydrogen, the transmittance decreases by 0.85 at 1200 seconds. The transmittance reaches to saturated value, keeping the exposure. It is considered that the gasochromic coloration level does not change by the concentration of hydrogen, but corresponds to the amounts of hydrogen which reach at the tungsten oxide thin film [6]. On the other hand, the delay of the reduction happens in N_2 atmosphere. The gasochromic coloration of the tungsten oxide thin films is supposed to change by the species and the composition of element in atmosphere.

When the transmittance is decreases to the lower than 0.5, half of the full coloration, the change of the color in the tungsten oxide thin films can be recognized by viewing. On the tungsten oxide thin film deposited on the PET sheet substrate, the time in the case of the exposure with 1, 0.5, 0.1, and 0.05 % hydrogen is 18, 46, 100, 381 seconds, respectively. In this examination, it is concluded that the hydrogen of diluted concentration until 0.1 can be detected within few minutes with the tungsten oxide thin films % by viewing, and can be applied to the sheet-type hydrogen sensor.

4. CONCLUSIONS

The deposition of the tungsten oxide thin films on the polymer sheets was performed with various O_2 partial pressures at room temperature, using the reactive r.f. sputtering method. At the O_2 partial pressure of 18 mPa, the deposition rate is 14 nm/min and the tungsten oxide thin film has maximum of the gasochromic coloration level. To expose 1 % hydrogen, the tungsten oxide thin films deposited on the polymer sheets with the deposition rate is 14 nm/min change the color more than 50 % within 20 seconds. The hydrogen of diluted concentration until 0.1 % can be detected within few minutes with the tungsten oxide thin films deposited on the PET sheet substrate by viewing with the naked eye. The tungsten oxide thin films can be applied to the sheet-type hydrogen sensors which is able to use repeatedly.

ACKNOWLEDGMENTS

This work was partly supported by a Grant-in-Aid for Scientific Research(C) from the Japan Society for the Promotion of Science (No.17560625).

REFERENCES

[1] K. Ito and T. Ohgami, *Appl. Phys. Lett.*, **60**, 938-40 (1992).
[2] Yong-su Oh, Junichi Hamagami, Yuichi Watanabe and Masasuke Takata, *Sensors and Actuators B*, **14**, 547-48 (1993).
[3] D. Schweiger, A. Georg, W. Graf, V. Witter, *Solar Energy Materials and Solar Cells*, **54**, 99-108 (1998).
[4] H. Nakagawa, N. Yamamoto, S. Okazaki, T. Chinzei, S. Asakura, *Sensors and Actuators B*, **93**, 468-74 (2003).
[5] S. Sumida, S. Okazaki, S. Asakura, H. Nakagawa, H. Murayama, T. Hasegawa, *Sensors and Actuators B*, **108**, 508-14 (2005).
[6] K. Takano, S. Yamamoto, M. Yoshikawa, A. Inouye, A. Sugiyama, *Trans. Mater. Res. Soc. Jpn.*, **31**, 223-30 (2006).
[7] C. Christofides, A. Mandelis, *J. Appl. Phys.*, **68**, R1-30 (1990).
[8] Ji-Guang Zhang, David K. Benson, C. Edwin Tracy, Satyen K. Deb, and A. W. Czanderna, *J. Electrochem. Soc.*, **144**, 2022 (1997).
[9] C. Bechinger, M. S. Burdis and J. –G. Zhang, *Solid State Commum.*, ***101***, 753-56 (1997).
[10] M. Stolze, B. Camin, F. Galbert, U. Reinholz, L.K. Thomas, *Thin Solid Films*, **409**, 254-64 (2002).
[11] A. Georg, W. Graf, V. Wittwer, *Electrochemica Acta*, **46**, 2001-05 (2001).
[12] V. Vitry, F. Renaux, R. Gouttebaron, J.-P. Dauchot, M. Hecq, *Thin Solid Films*, **502**, 265-69 (2006).

(Received January 20, 2007;Accepted May 10, 2007)