Transactions of the Materials Research Society of Japan 31[1] 223-226 (2006)

High Sensitive Gasochromic Hydrogen Sensors using Tungsten Oxide Thin Films

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A fiber optic hydrogen (H_2) sensor using a tungsten oxide (WO_3) thin film which has a gasochromic property for hydrogen has been developed in this investigation. The WO_3 thin films with the oriented crystal structure coated by the palladium were fabricated by reactive rf magnetron sputtering in slight oxygen atmosphere, O_2/Ar = 10%, on quartz substrate at 600 °C. The film colors 40%/sec for 1% H_2. This high gasochromic coloration rate is caused by the oriented crystal structure of WO_3. It is revealed that the crystallinity dependence of gasochromic coloration mechanism is different from that of the electrochromic coloration. The fiber-optic H_2 sensor was developed for detection of the leak H_2 using the WO_3 thin film and conventional optical fibers. The fiber-optic H_2 sensor in normal ambient air at room temperature can operate very well such as the transmittance promptly decreases by 15%/sec for blowing the rarefy H_2 of which the concentration is less than 1%. The property the sensor of meets the requirements of the H_2 sensors for practical use.
Key words: Tungsten Oxide, Hydrogen, Gasochromic, Hydrogen Sensors, Optical Fiber

1. INTRODUCTION

The development of a hydrogen (H_2) sensors has been prompted by the potential use of hydrogen fuel in various applications, monitoring pipeline corrosion and surveillance of battery recharging [1-4]. The dangers associated with the use and storage of hydrogen has always been a tremendous problem. A leak of gaseous hydrogen in air, at room temperature and atmospheric pressure, leads to an easily ignited explosive atmosphere for hydrogen concentrations by volume of more than 4%, the lower explosive limit [5]. For this reason, it has been required highly sensitive hydrogen sensor detectors to prevent accident due to H_2 gas leakage.

Most of hydrogen sensors are based on a detection of electrical resistance with semiconductor [3, 5], and then has high sensitivity and rapid response, but has some problems, consuming large power for device heating on high-temperature to operate, complex construction for electric circuits, and heavy weight. The fiber optic sensors using tungsten oxide (WO_3) thin films which has gasochromic property for H_2 have been investigated so that the fiber optic sensors and it's systems have less power, more light weight, and smaller size, simpler structure than the electrical sensors [1, 2, 4, 6]. But the response for H_2 is very slow that are minutes order.

The optical sensing characteristic is measuring the gasochromic coloration, i.e., the change of optical transmittance of WO_3 thin film. However the physical mechanism of the gasochromic coloration is still not fully understood despite the recent detailed studies. The gasochromic coloration mechanism of WO_3 has been considered to relate to the double injection of electrons and protons into the films, which can be written in a simplified form as [7]

$$xH^+ + xe^- + WO_3 \Leftrightarrow H_x WO_3 \quad (1),$$

as regarded as being similar to an electrochromic coloration mechanism. Kaneko et al. reported the crystallinity dependence of the electrochromic coloration that the crystalline WO_3 films have a higher coloration rate than amorphous film, while the WO_3 thin films with the oriented crystal structure have lower coloration rate than amorphous film [8]. The crystallinity dependence of the gasochromic coloration is not cleared, so as the investigations of the property have been reported about almost amorphous WO_3. Georg et al. proposed that the gasochromic coloration is depended on a pore surface of WO_3 thin films which have amorphous or columnar crystal structure [9, 10]. In the oriented crystal structure with column which has a large surface, it is expected that adsorbed H_2 easily diffuses to the surface, and then the gasochromic property could be improved.

In this paper, WO_3 thin films with an oriented crystal structure are fabricated with sputtering method, and the gasochromic coloration ratio for H_2 is measured by time resolve measurement of the optical transmission. Then a fiber-optic H_2 sensor, which has simple mechanism monitoring of the transmittance with 650 nm light, was constructed with the WO_3 thin film. The demonstration was performed with assuming a practical condition.

2. EXPERIMENTAL PROCEDURE

2.1 Sample preparation

The WO_3 thin films were fabricated by a reactive radio frequency (rf) magnetron sputtering with a tungsten (W) metal target. The base pressure was less than $1x10^{-5}$ Pa. The WO_3 thin films were deposited on

0.5 mm thickness Quartz substrate at 600 °C in a mixture atmosphere of oxygen (O_2) and argon (Ar). The gas composition was adjusted to the ratio O_2/Ar = 10% by two mass-flow controllers with a constant O_2 flow of 15 sccm and Ar flow 95 sccm. The total pressure was maintained 160 mPa. The deposition of WO_3 was performed for 30 minutes with rf power 50 W after pre-sputtering for 5 minutes. Then the film thickness was 0.5 um, and the deposition rate is 0.28 nm/sec. The color of the WO_3 thin films has transparent yellowish green.

The crystal structure of the WO_3 thin films were identified by x-ray diffraction (XRD) measurement using the Cu $K\alpha$ radiation in Bragg reflection geometry.

Since palladium (Pd) metal can be used as catalyst materials facilitate the reaction with H_2 [5], Pd metal was sputtered onto the WO_3 surface. The deposition of Pd was performed for 2 minutes with rf power 50 W, in Ar atmosphere 150 mPa after pre-sputtering for 5 minutes. Then the film thickness was 30 nm, and the deposition rate is 0.25 nm/sec. The density distributions and the thickness of the Pd and the WO_3 in the sample were also characterized with Rutherford Backscattering Spectrometry (RBS) at JAEA, TIARA. The film was confirmed to have the sharp interface between the Pd and the WO_3. The surface morphology of the Pd deposited WO_3 thin films were observed by the scanning electron microscopy (SEM).

2.2 Measurement of gasochromic property

To characterize the gasochromic property for H_2, the optical transmission of the Pd deposited WO_3 thin film was measured by time resolved optical spectroscopy at room temperature. A measurement set up has been constructed as depicted in Fig. 1. The main part is the sealed gas cell where the surrounding gas atmosphere could be changed from air to diluted hydrogen gas which is fixed density, and the flow rate of the gas can be stable. The sample was put in the cell, and is exposed to a diluted hydrogen gas, 1% H_2 in 99% Ar, which is introduced into the gas cell with 70ml/min by use of the corresponding valves. The 650 nm red light from a light-emitting diode, is transmitted the film, and detected by the spectrometers.

To obtain comparable information, the transmittance T has to be defined by applying $T=I/I_0$, where I_0 and I are the intensity of transmitted light in air and in diluted H_2 atmosphere, respectively. The I_0 and I was subtracted the background of the spectrometers.

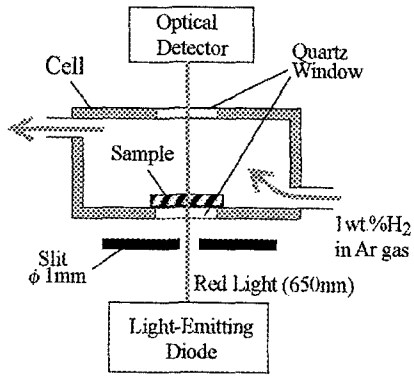

Fig. 1. Configuration for measurement of response for samples. The sample was put into gas shielded cell.

2.3 Construction of prototype fiber-optic H_2 sensor

A prototype fiber-optic H_2 sensor based on coloration of a WO_3 thin film was constructed with conventional optical fibers in which the diameter of the core is 50 μm, as depicted in Fig. 2. The H_2 which is Pd deposited WO_3 thin film is exposed to normal ambient air. The 650 nm red light, of which the power is less than 1 mW emitted from a semiconductor laser, is monitored by the photo diode without an optical chopper and a lock-in amplifier, through the frontward optical fiber cable, the hydrogen detector, and the backward optical fiber cable.

The demonstration of the detection of leaked H_2 was performed at room temperature. A diluted hydrogen gas, 1% H_2 in 99% Ar was blown to the H_2 detector with pumping the balloon in softly, keeping the distance of 3cm. The concentration of H_2 will rarefy to less than 1% to reach at the H_2 detector, because H_2 has a large diffusion coefficient 0.61 cm/s in air [4].

3. RESULTS AND DISCUSSION

3.1 Structure

The crystal structure of the WO_3 thin film without Pd catalyst was confirmed with XRD analysis as seen in Fig. 3. Two peaks are observed at diffraction angle 2θ = 23 degree, and 47 degree. The peak at 23 degree is very strong. These peaks might be attributed to a monoclinic or an orthorhombic phase WO_3 [11]. These peaks can be assigned to the (002) and (004) monoclinic plane. The monoclinic phase WO_3 has lattice parameters that are nearly identical to the orthorhombic phase. These two phases cannot be distinguished within the accuracy of the XRD data. Therefore, we will continue to refer to both this monoclinic and orthorhombic phase. In this report, the WO_3 thin film is assumed to be the monoclinic phase as simply. The WO_3 thin film has the (001) oriented crystal structure. The WO_3 thin film is supposed to have a porous and nonstoichiometric WO_3 thin film, i.e., WO_{3-x} [8], or to consist of is larger columnar crystallites which grown toward the vertical against to substrate [9, 12].

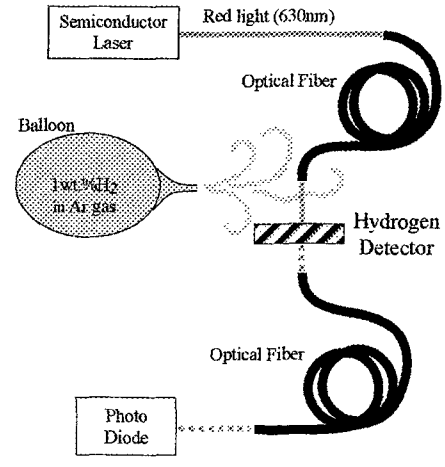

Fig. 2. Schematic diagram for a fiber optic H_2 sensor testing. The detector is exposed in normal ambient air.

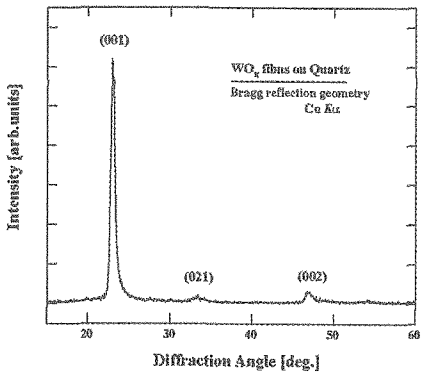

Fig. 3. X-ray diffraction patterns of the rf sputtered tungsten oxide thin film on quartz substrate at 600 degree centigrade formed in an Ar-10%O_2 gas mixture.

After Pd catalyst deposited on the WO_3 thin films with the oriented crystal structure, the surface morphology was observed by SEM. The SEM image was shown in Fig. 4. The surface of the film consists of the Pd grains about 20 nm in diameter. The surface of the WO_3 thin film with the oriented crystal structure is supposed to be not smooth, so that the deposited Pd grown like an island. It is expected to cause many adsorption of H_2 to the large surface of Pd, and much injection of electrons and protons into the WO_3 thin films.

3.2 Gasochromic property

The gasochromic coloration ratio of the WO_3 thin film was measured with sealed gas cell, as shown in Fig. 5. As soon as the film is exposed to 1% H_2, the transmittance drops down rapidly less than 60%/sec, and then, decrease exponentially to less than 10% for 7 seconds, to less than 1% at the finally. The film colors from transparent yellowish green to transparent dark blue, because the red light is absorbed [14]. The response time is shorter, and saturated transmittance is lower than amorphous film with similar condition [13, 14]. This result is different from the crystallinity dependence of the electrochromic coloration [8]. Therefore the mechanism of gasochromic coloration is considered to be different from that of the electrochromic.

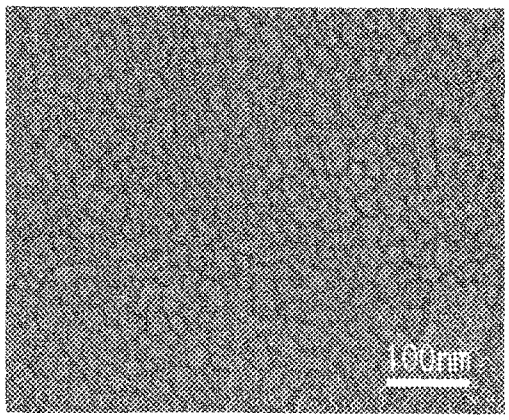

Fig. 4. SEM image of WO_3 thin film with an oriented crystal structure on which 30nm Pd catalyst deposited.

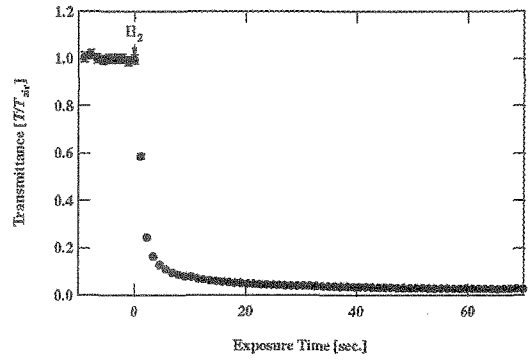

Fig. 5. Gasochromic property for 1 % H_2 of WO_3 thin film with the oriented crystal structure coated by Pd layer with 30 nm thickness.

Monitoring the transmittance of the WO_3 thin film using the red light can be expected to detect 1% H_2 within 1 second. The reasons why the coloration is rapid is considered that the much hydrogen can adsorb in the large surface area of Pd on the thin film, and the electrons and protons can easily diffuse or inject into to WO_3 oriented crystal, though the interface between Pd and WO_3.

3.3 Demonstration of prototype fiber-optic H_2 sensor

The fiber-optic H_2 sensor was constructed with the WO_3 thin film which has the oriented crystal structure coated by the Pd. Fig. 6 shows the typical result of test which was performed at room temperature in normal ambient air blowing the diluted hydrogen gas to the hydrogen detector for several times.

The First blowing of the diluted hydrogen gas for less than 1 second causes a prompt decrease of the transmittance to 0.85 for 0.6 seconds through the coloring detector, as exposure. The ratio of first detection signal is 15%/sec, which is much larger than that of the noise in signal. The fiber-optic hydrogen sensor can detect the rarefied H_2 in air, less than 1 %, within 1 second. The efficiency of the fiber-optic hydrogen sensor is enough to detect the leak practicably.

As soon as the first blowing stop, The coloration is stop, then the transmittance recovers to 0.93 for 9.4 seconds logarithmically. The de-colorization of the detector is slower speed than the coloration.

Second blowing causes a prompt decrease of the transmittance from 0.93 to 0.50 for 2 seconds in blowing. The dropped margin of second detection signal is 43%, which is three times as large as that of the first detection signal. It is considered that the dropped margin of detection signal corresponds to the amounts of hydrogen which reach at the detector. The amount of hydrogen to reach at the H_2 detector could be estimate from the margin of detection signal in the fiber-optic H_2 sensor. Thus, the coloration ratio of the sensor is more than ten times in previous report with similar condition [6], and could be estimate the concentration, quantitavely.

4. CONCLUSION

The WO_3 thin films with the oriented crystal structure were fabricated by reactive rf magnetron sputtering in slight oxygen atmosphere, O_2/Ar = 10%, on quartz substrate at 600 °C. The films color 40 %/sec for 1%

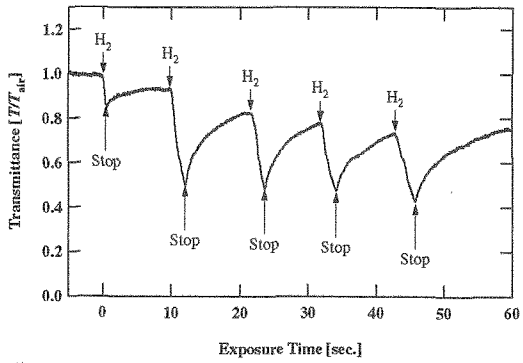

Fig. 6. Response of a fiber-optic hydrogen sensor for blowing of 1% H_2 in normal ambient air at room temperature. The detector of this sensor was constructed with a WO_3 thin film with the oriented crystal structure coated by the Pd.

hydrogen. This high gasochromic coloration rate is caused b y the oriented crystal s tructure of WO_3. This crystallinity dependence of gasochromic coloration mechanism is different from that of the electrochromic coloration.

Using t he WO_3 thin film with t he oriented crystal structure as the optical H_2 detector, a fiber-optic H_2 sensor was developed for detection of the leak H_2. The fiber-optic H_2 sensor in normal ambient air at room temperature can function very well such as the optical transmittance promptly decreases by 15%/sec for blowing the rarefy H_2 of which the concentration is less than 1%. The property meets the requirements of the H_2 sensor for practical use, as shown in Table 1. In future, the fiber-optic sensor will be required for each test, gas selectivity from interference gases such as hydrocarbons, durability and so on.

ACKNOWLEDGMENT

This study was supported by Grant-in-Aid for Young Scientists (B) (No. 16760591).

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Sensitivity	< 1 %H_2
Operating Temperature	R.T.
Response Time	< 1 sec.
Coloration Rate	> 50%
Detection Signal Accuracy	< 5%
Gas environment	Ambient air

Table 1. Requirements of the hydrogen sensor for practical use.

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(Received December 11, 2005; Accepted January 15, 2006)