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Low-Temperature Formation of a WO₃ Thin Film by the Sol-Gel Method Using Photo-Irradiation and Fabrication of a Flexible Hydrogen Sensor

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Abstract

Hydrogen has been recently attracted much attention with respect to high energy-conversion efficiency and low environmental burden. However, hydrogen gas is dangerous due to an explosive gas and a fast combustion rate. Therefore, the development of hydrogen sensor with high accuracy and reliability that can detect hydrogen easily is required. Especially, a flexible hydrogen sensor is useful because it has a high degree of freedom with respect to the shape of location in which the sensor is to be located. A flexible hydrogen sensor—namely, a WO₃ thin film formed on a PET film by the sol-gel method using photo irradiation—based on gasochromism of WO₃ was developed. By irradiating a thin film, which was prepared by using WO₃ precursor solution synthesized by the sol-gel method, with ultraviolet rays, a high-purity WO₃ film could be prepared on PET at low temperature. The sensor was structured as a polystyrene (PS) film containing palladium (Pd) laminated on a WO₃ film. The WO₃ layer was porous, so the PS containing Pd atoms solution penetrated the WO₃ layer. WO₃ reacted with hydrogen gas and instantly turned blue as the transmittance of the WO₃ layer changed. The sensor showed high reactivity even for hydrogen concentration below 4% (1%, 0.5%, 0.25%, and 0.1%), which was the lower limit of hydrogen ignition, and a linear relationship between hydrogen concentration and change in transmittance was found. Moreover, the resistance of the WO₃ film significantly and instantaneously changed due to hydrogen-gas exposure, and the hydrogen concentration and resistance change showed a linear relationship. It is therefore possible to quantitatively detect low concentrations of hydrogen by using changes in transmittance and resistance as indices. Since these changes occur selectively under hydrogen at room temperature and normal pressure, they form

the basis of a highly sensitive hydrogen sensor. Since the developed sensor is flexible, it has a high degree of freedom with respect to the shape of location in which the sensor is to be installed.

1. Introduction

In recent years, owing to the problems of global warming due to mass consumption of fossil fuel and the depletion of energy resources, development of alternative energy sources as a replacement for fossil energy has become urgent. Among those energy sources, hydrogen is attracting attention because it can be produced from various raw materials, such as LNG, fossil fuels, biomass, and water, and it has a "clean" advantage; namely, only water is discharged during its combustion [1] [2].

A fuel cell—which uses hydrogen as an energy source—is a highly efficient energy system capable of converting chemical energy of hydrogen directly into electric energy. In addition, since fuel cells emit neither harmful gases (such as carbon dioxide) due to incomplete combustion nor exhaust gases (such as those generated by combustion of fossil fuels), they are gaining much attention from the viewpoint of their environmental friendliness. Accordingly, from now onwards, fuel cells are expected to be rapidly developed as power sources for fuel-cell vehicles as well as stationary power sources [3] [4]. A sensor that detects leakage of hydrogen (which is highly explosive) is an indispensable technology in regard to the development of fuel cells. In particular, in places where hydrogen gas is compressed and stored at a high pressure, such as a fuel-cell vehicle or a hydrogen filling station, a sensor for selectively detecting hydrogen leakage with high sensitivity is required. Hydrogen leaks easily because it is the smallest molecule, and it has a wide combustion range; in particular, its minimum ignition energy in the air is extremely low, namely, one-tenth that of methane, gasoline, etc. Consequently, when ignited, hydrogen explodes catastrophically; in other words, it is an extremely dangerous gas. For that reason, there is a strong demand for a sensor that can detect hydrogen leakage (in consideration of a hydrogen-explosion limit of 4% or less) with high sensitivity and selectivity. And also, a flexible sensor for detecting hydrogen gas which can be located on complex shape substrates such as a hydrogen gas stored spherical tank and a cylindrical pipe, etc., is required.

Conventional hydrogen sensors include catalytic-combustion gas sensors and metal-oxide-semiconductor gas sensors; however, they face two problems: 1) high operating temperature (400˚C or higher) and 2) low gas selectivity [5]. Since the sensor operates at high temperature, the substrate on which the ele-

ment for sensing hydrogen gas is formed is limited to one with high heat resistance (such as a ceramic or glass), and it is difficult to use an organic resin as a substrate because it has no heat resistance. In the case of thin-film sensors, physical deposition methods, such as sputtering and vacuum evaporation method, are generally used for fabricating the sensors [6]-[11]; however, it is problematic that these methods use large, high-vacuum facility, thereby increasing manufacturing costs. As a low-cost method, forming a tungsten trioxide (WO_3) thin film by coatings of a solution by using the sol-gel method has been reported [12] [13] [14] [15]. It has also been reported that when platinum (Pt) or palladium (Pd) is included in the WO_3 film as a catalyst, it reacts with hydrogen molecules at room temperature, and the optical properties and conductivity of the film change significantly. Accordingly, a hydrogen sensor using that change in properties has been proposed. Nishio *et al.* reported that a WO_3 film containing Pt can be produced by the sol-gel method, and the film showed high reactivity to hydrogen gas [16]. Moreover, S. Fardindoost *et al.* reported that a WO_3 thin film doped with Pd can be formed by the sol-gel method, and the resistance of the film changes significantly on contact with hydrogen gas [17]. In both cases, heat treatment at high temperature was used to produce the WO_3 films, and both films were formed on a substrate with high heat resistance, such as glass or alumina. To obtain an inorganic thin film with high purity by using the sol-gel method, heat treatment of about several-hundred degrees Celsius is usually required [18]. For that reason, it is difficult to use an organic-resin substrate because it has low heat resistance. In order to develop a flexible hydrogen sensor, the technique is required for low temperature formation method of WO_3 film on organic-resin substrate. To best our knowledge, there is no report on sol-gel derived WO_3 thin film with high quality on organic film.

In this paper, regarding our aim of manufacturing a high-sensitivity hydrogen sensor with flexibility at low cost, 1) the development of low-temperature technology for depositing a WO_3 film by the sol-gel method with photo-irradiation and 2) forming the WO_3 film on a PET film to form a flexible hydrogen sensor are reported.

2. Experimental

2.1. Fabrication of PS (Pd)-Laminated WO_3 Thin Film

A polystyrene (PS) thin film containing palladium (Pd) was formed on a WO_3 thin film formed by photo irradiation; as a result, a PS(Pd)/WO_3 thin film with a laminated structure was produced. Under a nitrogen atmosphere, 1.196 g of WCl_6 (Sigma-Aldrich) was dissolved in 6 ml of dehydrated ethanol to prepare a 0.5M solution. This solution was spin-coated (3000 rpm for 30 s) on a PET film (30 mm × 30 mm; thickness: 100 μm; Toyobo Co. A7300). The spin coating was performed inside a glove box with humidity kept at about 50% by a humidifier. Subsequently, the WO_3 precursor film formed on PET was irradiated with ultraviolet rays (wavelength: 254 nm and 185 nm; light intensity: 12 mw/cm^2) at

100°C for 20 minutes. This thin-film-formation process was repeated three times to increase the thickness of the WO_3 thin film. Pd $(CH_3COO)_2$ (Kanto Chemical Co.) was added to a 10 wt% PS (Wako Pure Chemical Co.: Degree of polymerization 2000) toluene solution to prepare a solution containing 1 wt% of Pd. This solution was spin-coated on the WO_3 thin film (at 3000 rpm for 30 s) and then dried at 100°C for 10 minutes.

Moreover, a PS(Pd)/WO_3 laminated thin film was formed on a PET film, on which a Ti/Pt electrode was formed, by the same method described above, and that film was used as a sample for measuring change in resistance during exposure to hydrogen.

2.2. Evaluation of Hydrogen Sensitivity of Thin Film

The PET film coated with the PS(Pd)/WO_3 laminated film was cut into a 8 × 24-mm, which was then placed in a 1-cm cell for spectrophotometer measurement, and the upper part of a cell was covered with polydimethylsiloxane (PDMS).

Two injection needles were inserted into the cell, and hydrogen (of a predetermined concentration) was introduced through one of the needles and discharged from the other. The inside of the cell was filled with a hydrogen atmosphere at constant concentration. As for the hydrogen, a nitrogen-hydrogen mixed gas (hydrogen concentration: 0.1%, 0.25%, 0.5%, 1.0%, and 4%; Japan Fine Products) was used. Change in transmittance of the thin film when hydrogen gas was introduced was measured by spectrophotometer (Shimadzu UV3600). Dry air was used for discharging the hydrogen gas, and a three-way cock was used to switch between hydrogen gas and dry air.

With respect to the resistance change at the time of hydrogen exposure, the resistance change of the PS(Pd)/WO_3 laminated thin film formed on the PET film (on which the Ti/Pt comb-shaped electrode was formed) was tracked by using a resistivity meter.

2.3. Evaluation of Film

The chemical structure of the WO_3 film was investigated by measuring its infrared absorption spectrum (Shimadzu FT-IR8400S). The surface of the thin film was observed by optical microscope (Kyowariken ME-LUX2) or digital microscope (Keyence VHX-500F) as well as by scanning electron microscope (SEM: Carl Zeiss ULTRA55). The cross-sectional structure of the PS(Pd)/WO_3 film was observed by transmission electron microscope (TEM: HITACHI HF-2000). The samples for these observations were fabricated by FIB (focused ion beam) processing.

3. Results and Discussion

3.1. Hydrogen Sensor Using WO_3 Thin Film

The WO_3 thin film was used as an element for detecting hydrogen, and the "ga-

sochromism" property of the thin film was used. The detection principle is shown schematically in **Figure 1**. Although WO_3 is colorless and transparent, tungsten bronze (HxWO₃) is formed by incorporating H^+ ions into the WO_3 and thereby color it blue. By incorporating H^+ in the structure of WO_3, the valence of W changes to a mixed valence state composed of W^{6+} and W^{5+}. At that time, absorption based on intervalence charge-transfer transitions appears extensively in range from the visible-light region (around 450 nm) to the near-infrared-light region (around 2000 nm) [19]. The thin film turns blue due to absorption of light in the visible-light region. At that time, electrons are conducted between the W^{5+} and W^{6+} states by hopping conduction, so that the electrical characteristics of the WO_3 thin film change, and its insulating property changes to conductive. Pd was used as a catalyst for dissociating hydrogen molecules into hydrogen atoms. The catalytic effect of Pd and Pt is well known as so-called spillover effect [20]. The hydrogen atoms dissociated on the Pd are induced into the WO_3 film by the spillover effect, and tungsten bronze is generated. On the contrary, in the absence of hydrogen, the Pd promotes the reaction between the Hx of HxWO₃ and atmospheric oxygen, so it plays a role as a catalyst for generating H_2O and WO_3. Since this reaction is a reversible according to the presence or absence of hydrogen, hydrogen can be detected by the coloring of the WO_3 thin film. Since this reversible reaction occurs at room temperature and selectively reacts with only hydrogen molecules, it is possible to develop a high-sensitivity hydrogen sensor that operates at room temperature.

3.2. Low-Temperature Fabrication of WO₃ Thin Film by the Sol-Gel Method Using Photo Irradiation

The sol-gel method was used for producing the WO_3 thin film. As for this method, a precursor of an inorganic polymer is generated by chemical reactions (hydrolysis and polycondensation) in a solution, and the precursor is applied to a substrate and heat-treated to form an inorganic thin film. The general sol-gel method requires heat treatment of several hundred degrees in order to cure and
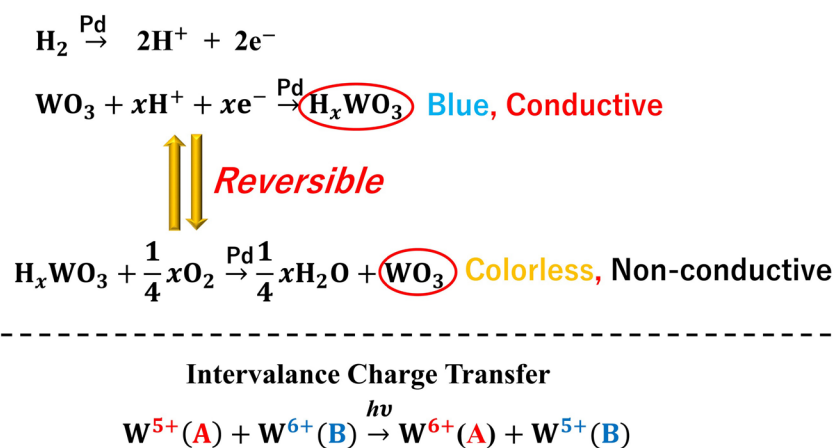
$$H_2 \xrightarrow{Pd} 2H^+ + 2e^-$$

$$WO_3 + xH^+ + xe^- \xrightarrow{Pd} H_xWO_3 \quad \text{Blue, Conductive}$$

$$\Updownarrow \quad \textit{Reversible}$$

$$H_xWO_3 + \frac{1}{4}xO_2 \xrightarrow{Pd} \frac{1}{4}xH_2O + WO_3 \quad \text{Colorless, Non-conductive}$$

Intervalance Charge Transfer

$$W^{5+}(A) + W^{6+}(B) \xrightarrow{h\nu} W^{6+}(A) + W^{5+}(B)$$

Figure 1. Hydrogen detection principle using gasochromism of WO_3.

densify the thin film [18]; however, as for the sol-gel method used in this study, photo irradiation was used for curing the thin film. This method is effective for forming an inorganic thin film at low temperature, and it can form an inorganic thin film on an organic-resin substrate (which has no heat resistance). It is reported that the sol-gel method using photo-irradiation gives various kinds of metal oxide films with good quality at low temperature [21] [22] [23] [24].

As the WO_3 sol-gel solution, tungsten alkoxide (produced by dissolving WCl_6 in ethanol) was used as the starting material. It has already been reported that WCl_6 produces tungsten alkoxide in alcohol [12]. $W(OC_2H_5)_6$ reacts with H_2O present in the solution or in the atmosphere to form a network structure composed of -O-W-O- bond by hydrolysis and polycondensation, resulting in the WO_3 precursor.

The sol-gel solution (serving as a WO_3 precursor) is applied to a PET-film (thickness: 100 μm) substrate, and it is irradiated with 254-nm (ultraviolet) light by using a low-pressure mercury lamp. The 254-nm light is almost coincident with the absorption wavelength of the metal-ligand charge-transfer absorption band of tungsten alkoxide $W(OC_2H_5)_6$, which is the starting material for forming WO_3. Since $W-OC_2H_5$ bond is selectively broken to yield W-OH species and form W-O-W bond by polycondensation, the production of inorganic polymer is promoted efficiently. After the sol-gel derived solution is spin-coated on a PET, the ozone and active oxygen generated in the atmosphere by the 254-nm ultraviolet irradiation penetrate into the film and promote the formation of the WO_3 thin film. At that time, if the substrate is heated to about 100°C, the diffusion of active oxygen into the film is accelerated, and a better-quality WO_3 film is obtained.

An infrared-absorption spectrum of the WO_3 film prepared by the above-described method is shown in Figure 2. The spectra of thin films prepared at room temperature, 50°C, and 100°C under photo-irradiation are also shown, and for the sake of comparison, the spectra of thin films dried at room temperature and heated at 300°C are also shown. The peak of stretching vibration of the generated WO_3-derived W-O-W bond appears around 650 - 820 cm^{-1}. Although in the dried product, absorption based on C-H stretching vibration of the alkoxy group is observed at around 2800 cm^{-1}, these absorptions were not observed in the case of the films irradiated at room temperature, 50°C, and 100°C, and strong absorption by W-O-W bond was observed around 650 - 820 cm^{-1}, suggesting the formation of WO_3. Furthermore, absorption by W-O-W bond became stronger with increasing temperature during photo-irradiation. The spectral pattern of the film photo-irradiated at 100°C is similar to that of the film heat-treated at 300°C, indicating that the structure of the photo-irradiated film at 100°C is similar to that of the 300°C-heat-treated film. It has been reported that a sol-gel film heat-treated at low temperature (about 100°C) shows absorption attributed to the W=O bond around 1000 cm^{-1} and disappears with increasing heat-treatment temperature to form a W-O-W network structure [14]. However, in the present study, such absorption was not observed in the case of a film produced by pho-

to-irradiation. This finding suggests that WO_3 is generated at a lower temperature by photo-irradiation.

3.3. Structure of Hydrogen Sensor

The structure, appearance, and hydrogen reactivity of the flexible hydrogen sensor are shown in **Figure 3**. A WO_3 thin film was formed on a PET film (film thickness: 100 µm), and a polystyrene (PS) thin film containing Pd was formed. The upper PS film functions as both a support layer of Pd (the catalyst) and a protective layer of the WO_3 thin film (the sensor layer). The PET film is flexible because its thickness is only 100 µm. Furthermore, the adhesion strength of the PS(Pd)/WO_3 film to PET was high, so the film did not peel off during a tape test
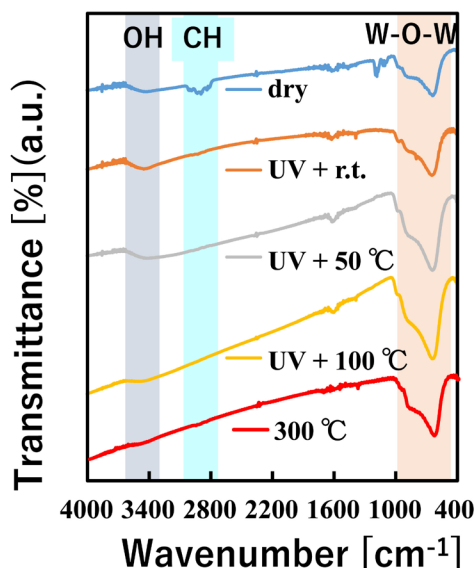
Figure 2. Infrared spectra of WO_3 films prepared by photo-irradiation.
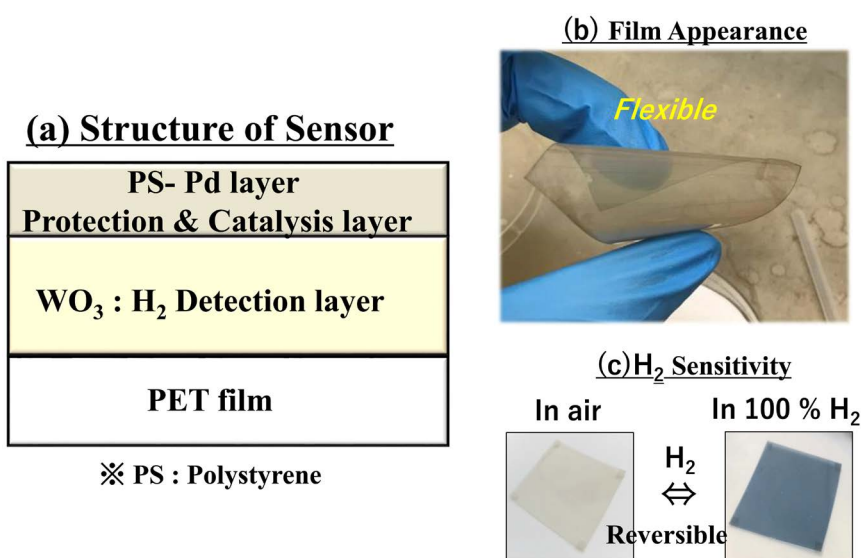

Figure 3. Structure, appearance and H_2 sensitivity of flexible H_2 sensor.

performed according to JIS standards (JIS K5600: Japan Industrial Standard). The film immediately turned blue in 100% hydrogen and showed high reactivity to hydrogen. Moreover, as soon as the film was re-exposed to air, the color disappeared, and the film returned to its original state.

SEM images of the surface state of the film are shown in Figure 4. The surface state of the WO_3 film (without PS formed as an upper layer) was porous with many cracks. In the case of the WO_3 film in which PS (Pd) was formed as an upper layer, cracks are reduced, and penetration of PS (Pd) into the WO_3 film is confirmed. Cross-sectional TEM observation images and the results of elemental analysis by EDX are shown in Figure 5. It can be seen that a WO_3 layer (thickness: about 600 nm), connected in the form of particles, is formed on the substrate, and a PS (Pd) layer (thickness: about 90 nm) is formed on top of the WO_3 layer. As for the WO_3 layer, since light and dark areas are observed, it can be said that this layer is in a porous state. As for the distribution of elements, although tungsten is observed to correspond to the WO_3 layer, since palladium and carbon
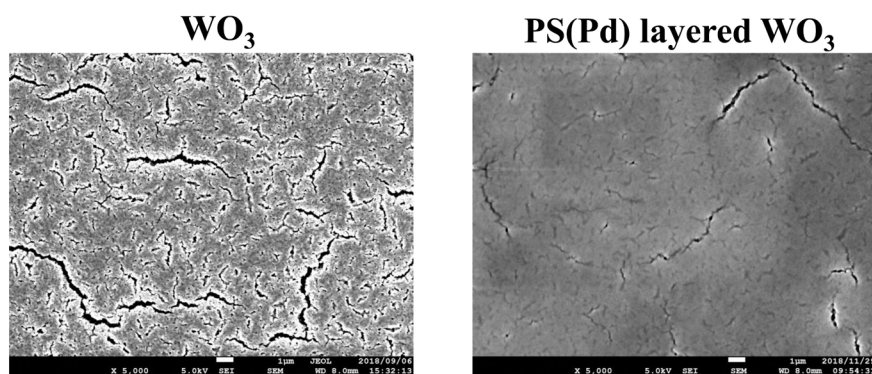

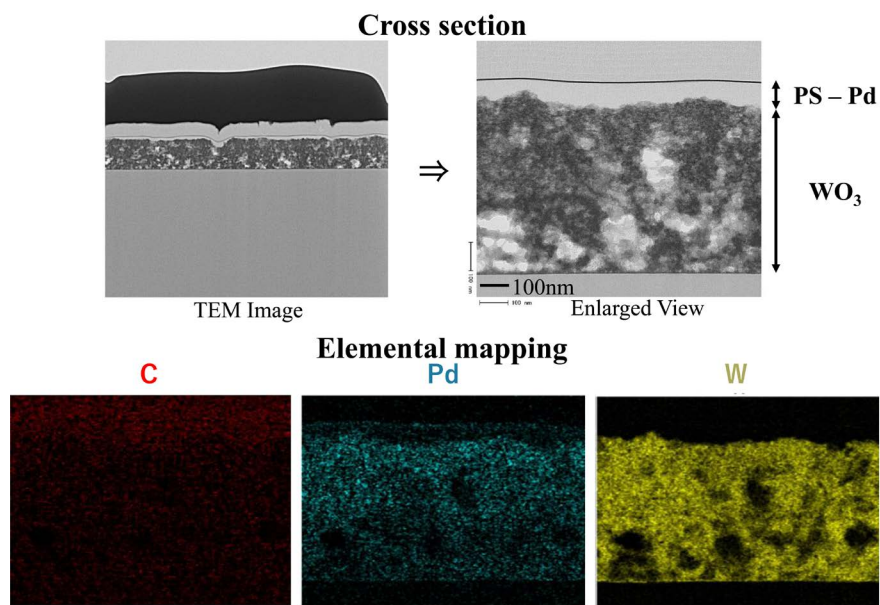**Figure 4.** Surface SEM images of WO_3 and $PS(Pd)/WO_3$ thin films.

Figure 5. Cross-sectional TEM images of $PS(Pd)/WO_3$ thin film and EDX analysis.

are also observed in the WO$_3$ layer, it is suggested that the PS(Pd) solution penetrates into the WO$_3$ layer. Since the specific surface area of the WO$_3$ layer is increased by the porous state, it is considered that the abundance of reaction sites with hydrogen is increased, so the film exhibits higher reactivity to hydrogen. It is assumed that since the PS solution containing Pd penetrates into the porous WO$_3$ layer, the Pd catalyst (exhibiting the spillover effect) is also dispersed in the WO$_3$ layer, and the reactivity between hydrogen atoms, which are generated form hydrogen molecules by Pd catalyst, and WO$_3$ is enhanced. In addition, PS plays a role of adhesion with the WO$_3$ particles and PET film, so it is considered to contribute to improving the strength of the hydrogen-sensor film. When the adhesive strength of the sensor film in regard to the PET film was examined by a tape-peeling test based on JIS standards (JIS K5600), it showed good adhesion of 100/100 (remaining number/cut number). Since PS has water repellency, it also has the effect of preventing deterioration of the WO$_3$ film due to water vapor and the like.

3.4. Transmittance Change with Hydrogen Concentration and Its Quantification

The reactivity to hydrogen of the PS(Pd)/WO$_3$ thin film appears in the change of its transmittance curve; accordingly, by tracking this change, it is possible to quantitatively evaluate hydrogen concentration. Change in the transmittance curve (in the 400 - 2000 nm region) of the PS(Pd)/WO$_3$ thin film when exposed to 100% hydrogen is shown in Figure 6. Under hydrogen exposure, the film instantly turned blue, and the transmittance from the visible-light region to the near-infrared region was greatly reduced due to the mechanism as shown in 3.1, indicating that by incorporating H$^+$ in WO$_3$ thin layer, the valence of W changed to a mixed valence state composed W^{6+} and W^{5+}. In particular, transmittance
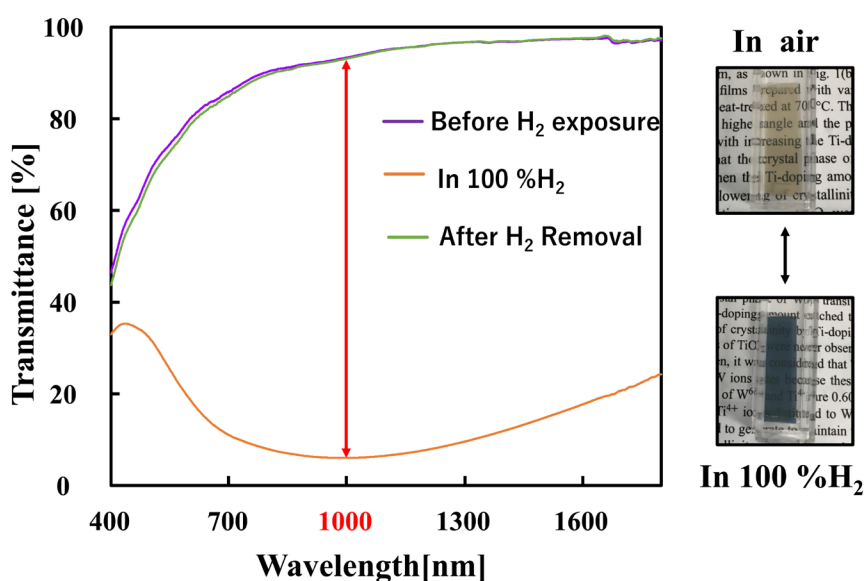

Figure 6. Transmittance spectra changes after exposure in 100% H$_2$.

was the lowest near 1000 nm, at which point the amount of change in transmittance was large. And transmittance decreased drastically—from 90% to 8%—by hydrogen exposure. When hydrogen was removed, the transmittance curve returned to its original shape, thereby confirming the reversibility of transmittance.

Change in transmittance at 1000 nm, at which the largest change in transmittance occurs, when hydrogen concentration is reduced from 4% (the lower explosion limit) to 1%, 0.5%, 0.25%, and finally to 0.1%, is shown in Figure 7. For any of the hydrogen concentrations, transmittance changed greatly when the hydrogen was introduced, and when the hydrogen was removed, it immediately returned to its original state (Figure 7(a)). The ultimate transmittance differs according to the hydrogen concentration, and the higher the hydrogen concentration, the larger the change in transmittance. Taking a log-log plot of the varying transmittance and hydrogen concentration reveals a clear linear relationship (Figure 7(b)). This result indicates that hydrogen concentration can be quantified by measuring the change in transmittance due to hydrogen exposure. The cycling characteristics of sensor performance due to hydrogen exposure are shown in Figure 8. This figure shows that the change in transmittance under hydrogen concentration of 4% and the recovery to the initial transmittance when the film is re-exposed to air are highly reproducible.

3.5. Change in Conductivity with Hydrogen Concentration and Its Quantification

A $PS(Pd)/WO_3$ laminated film was formed on a PET film on which a Ti/Pt comb-shaped electrode was formed, and the change in the resistance of WO_3 thin film on the PET film when exposed to hydrogen was measured. The appearance of the sensor and the results of the measurements are shown in Figure 9 and Figure 10, respectively. Cross-sectional SEM images are also shown in Figure 9.
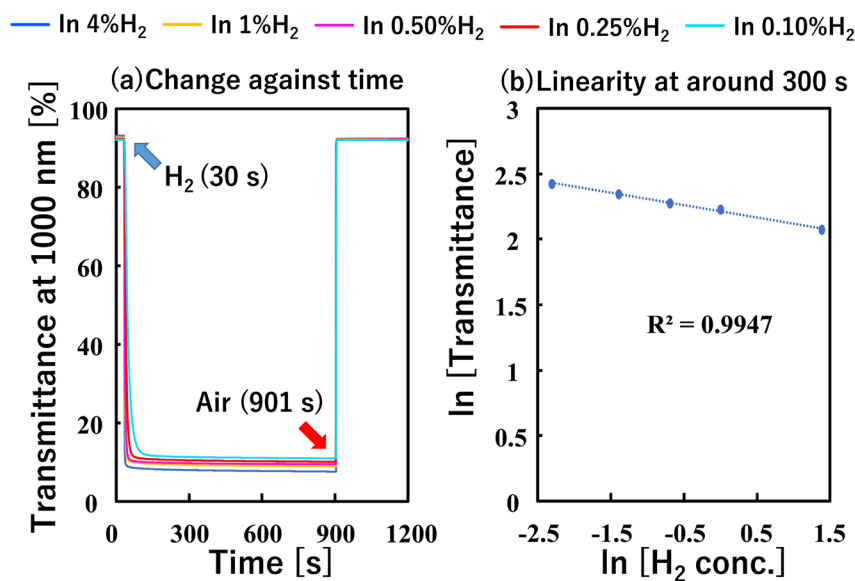

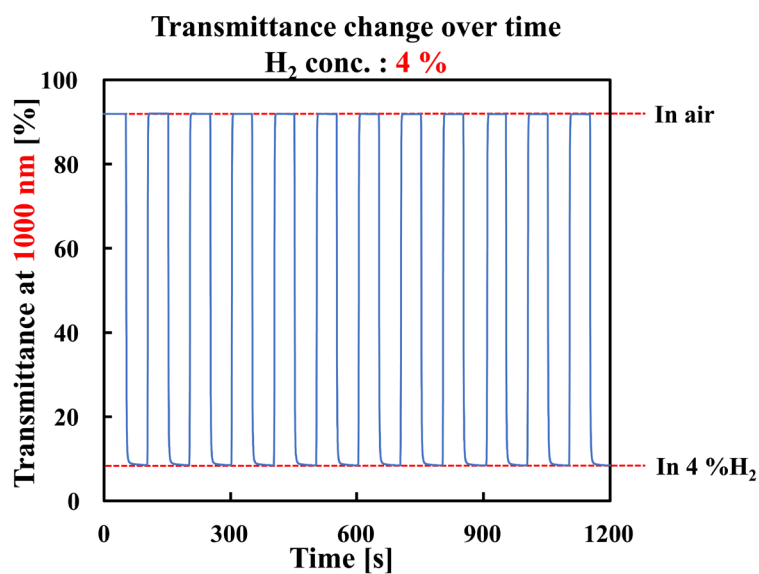Figure 7. Transmittance changes at 1000 nm after exposure in low concentration H_2.
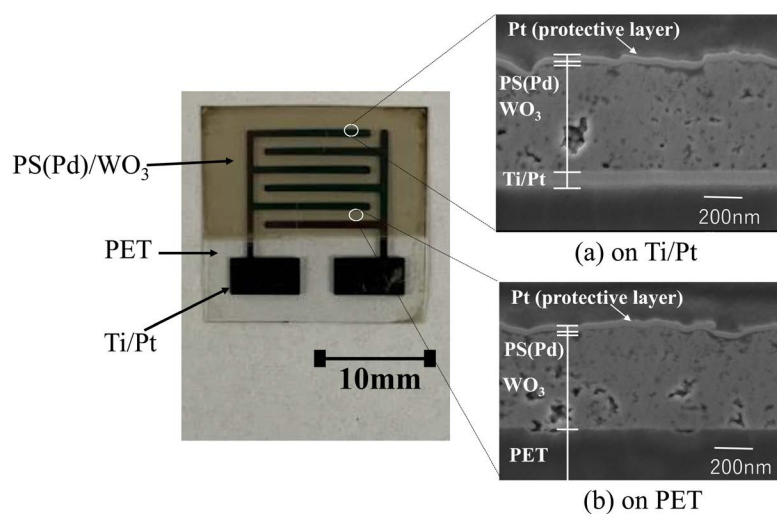
Figure 8. Repeated characteristics of H$_2$ exposure.

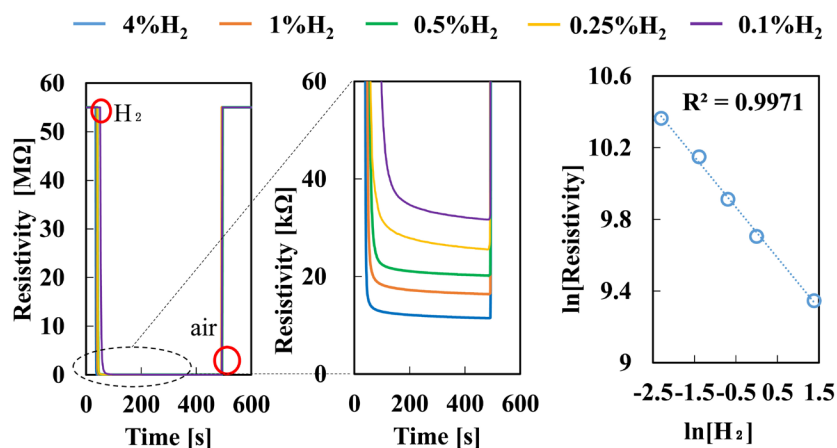**Figure 9.** PS(Pd)/WO$_3$ prepared on PET with TiPt electrode.

Figure 10. Resistivity changes after exposure in low concentration H$_2$.

Porous WO_3 layer with about 500 - 550 nm film thickness was observed on Ti/Pt electrode (**Figure 9(a)**) and PET (**Figure 9(b)**). Outermost layer of Pt is protective layer which was prepared when forming cross-sectional SEM sample for observation. When hydrogen was introduced, the resistance decreased significantly, and after 0.2 - 0.5 seconds, the value decreased from a state close to insulation resistance (55 MΩ) to 12 - 33 Ω due to hopping conduction of electron between W^{6+} and W^{5+} by forming the mixed valence state of W^{6+} and W^{5+}. And when the hydrogen was removed and air was introduced, the resistance state immediately returned to that close to the original insulation resistance. The log-log plot of the changed resistance (values after 300 s) when hydrogen at concentration of 4% to 0.1% was introduced against hydrogen concentration shows a good linear relationship. This result indicates that hydrogen concentration can be quantified from the change in resistance of the sensor.

As described above, the transmittance and resistance of the developed hydrogen sensor instantly change (in terms of color) even at low concentration of hydrogen, and the sensor is extremely sensitive to hydrogen. By incorporating both changes in transmittance and resistance due to hydrogen exposure into the sensor, it is possible to detect low-concentration hydrogen with high reliability. It is also possible to develop a flexible hydrogen sensor because the PS(Pd)/WO_3 laminated film can be formed on a flexible PET film at low temperature by the method (modified sol-gel using photo-irradiation) used in this study. By developing the compact flexible sensor which is integrated with the areas measuring transmittance change and resistivity change on the same PET film, hydrogen gas sensor with high accuracy and reliability would be possible.

3.6. Application of Flexible Sensors to Piping Systems

Since the hydrogen sensor formed on the PET film is flexible, it can be fitted in the form of a film sensor at sites with complicated shapes. The results of an experiment in which hole was formed in a cylindrical cardboard pipe (simulating real piping), the film sensor was installed on the pipe, and hydrogen was flowed into the cylindrical pipe are shown in **Figure 11**. It is clear from these results
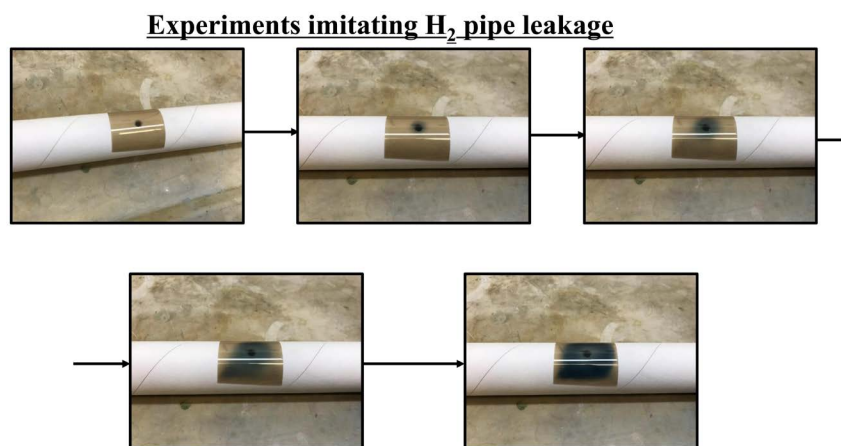
Experiments imitating H$_2$ pipe leakage

Figure 11. An example of application of flexible hydrogen sensor.

that the film sensor is gradually colored blue due to hydrogen leaking from the hole in the simulation pipe. The developed film sensor can thus be considered useful for visually detecting hydrogen leakage from piping of a hydrogen tank. A flexible hydrogen sensor has a high degree of freedom with respect to the location where it can be installed; therefore, it can be installed on complex shapes such as hydrogen tanks, and that capability will help to prevent explosions due to hydrogen leakage.

4. Conclusion

A flexible hydrogen sensor based on the gasochromism of WO_3 was developed by forming a WO_3 thin film on a PET film by the sol-gel method using photo irradiation. WO_3 reacted with hydrogen gas and instantly turned blue as its transmittance changed. High reactivity to hydrogen concentration below 1% (1%, 0.5%, 0.25%, and 0.1%), which is the lower limit for a hydrogen explosion, and a linear relationship between hydrogen concentration and transmittance were found. For that reason, it is possible to quantitatively detect hydrogen concentration. Moreover, the resistance of the WO_3 film also changed considerably and instantaneously due to hydrogen gas exposure, and the hydrogen concentration and resistance change showed a linear relationship. Accordingly, it is possible to quantitatively detect low concentrations of hydrogen even by using resistance change as an index. Since the developed sensor is flexible, it has a high degree of freedom with respect to the shape of the location in which it is to be installed. This sensor technology will contribute to ensuring safety against the risk of hydrogen leakage that will accompany the increasing spread of fuel cells and hydrogen filling stations in the future.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1]   Hydrogen Basic Strategy.
      http://www.meti.go.jp/press/2017/12/20171226002/20171226002-1.pdf

[2]   The Strategic Road Map for Hydrogen and Fuel Cells, Industry-Academia-Government Action Plan to Realize Hydrogen Society.
      http://www.meti.go.jp/press/2018/03/20190312001/20190312001-3.pdf

[3]   Ohira, E. (2013) The First Step for Realization of Hydrogen Society. *Journal of Fuel Cell Technology*, **13**, 1.

[4]   Saito, A. (2014) Future Prospects for Supply and Demand of Hydrogen Energy. *Journal of Fuel Cell Technology*, **14**, 9.

[5]   Kitaguchi, H. (2006) The Present Situation and Some Subjects of the Hydrogen Gas Sensor. *Journal of Fuel Cell Technology*, **6**, 91-99.

[6]   Eranna, G., Joshi, B.C., Runthala, D.P. and Gupta, R.P. (2004) Oxide Materials for Development of Integrated Gas Sensors—A Comprehensive Review. *Critical Re-*

views in Solid State and Materials Science, **29**, 111-188.
https://doi.org/10.1080/10408430490888977

[7] Sakai, G., Matsunaga, N. and Shimanoe, K. (2001) Theory of Gas-Diffusion Controlled Sensitivity for Thin Film Semiconductor Gas Sensor. *Sensors and Actuators B: Chemical*, **80**, 125-131. https://doi.org/10.1016/S0925-4005(01)00890-5

[8] Nakagomi, S., Okuda, K. and Kokubunn, Y. (2003) Electrical Properties Dependent on H2 Gas for New Structure Diode of Pt-Thin WO_3-SiC. *Sensors and Actuators B: Chemical*, **96**, 364-371. https://doi.org/10.1016/S0925-4005(03)00570-7

[9] Zhao, M. and Ong, C.W. (2012) Improved H_2-Sensing Performance of Nanocluster-Based Highly Porous Tungsten Oxide Films Operating at Moderate Temperature. *Sensors and Actuators B: Chemical*, **174**, 65-73. https://doi.org/10.1016/j.snb.2012.08.018

[10] Zhang, C., Boudiba, A., Oliver, M.-G., Synders, R. and Debliquy, M. (2012) Magnetron Sputtered Tungsten Oxide Films Activated by Dip-Coated Platinum for PPM-Level Hydrogen Detection. *Thin Solid Films*, **520**, 3679-3683. https://doi.org/10.1016/j.tsf.2011.12.085

[11] Sakaguchi, I., Saito, N., Watanabe, K., Adachi, Y. and Suzuki, T. (2016) Evaluation of Sensor Property for Hydrogen and Ethanol of Zinc-Doped Tin-Dioxide Thin Films Fabricated by RF Sputtering. *Journal of the Ceramic Society of Japan*, **124**, 714-716. https://doi.org/10.2109/jcersj2.16015

[12] Nishio, K., Sei, T. and Tsuchiya, T. (1999) Preparation of Electrochromic Tungsten Oxide Thin Film by Sol-Gel Process. *Journal of the Ceramic Society of Japan*, **107**, 199-203. https://doi.org/10.2109/jcersj.107.199

[13] Nakagawa, H., Yamamoto, N., Okazaki, S., Chinzei, T. and Asakura, S. (2003) A Room-Temperature Operated Hydrogen Leak Sensor. *Sensors and Actuators B: Chemical*, **93**, 468-474. https://doi.org/10.1016/S0925-4005(03)00201-6

[14] Yamaguchi, Y., Kineri, T., Fujimoto, M., Mae, H., Yasumori, A. and Nishio, K. (2011) Investigation of Electrical Hydrogen Detection Properties of Pt/WO_3 Thin Films Prepared by Sol-Gel Method. *Key Engineering Materials*, **485**, 271-274. https://doi.org/10.4028/www.scientific.net/KEM.485.271

[15] Yamaguchi, Y., Imamura, S., Ito, S., Nishio, K. and Fujimoto, K. (2015) Influence of Oxygen Gas Concentration on Hydrogen Sensing of Pt/WO_3 Thin Film Prepared by Sol-Gel Process. *Sensors and Actuators B: Chemical*, **216**, 394-401. https://doi.org/10.1016/j.snb.2015.04.020

[16] Fardindoost, S., Iraji zad, A., Rahimi, F. and Ghasempour, R. (2010) Pd Doped WO_3 Films Prepared by Sol-Gel Process for Hydrogen Sensing. *International Journal of Hydrogen Energy*, **35**, 854-860. https://doi.org/10.1016/j.ijhydene.2009.11.033

[17] Yamaguchi, Y., Nemoto, C., Ito, S., Nishio, K. and Fujimoto, K. (2015) Improvement of Hydrogen Gas Sensing Property of the Sol-Gel Derived Pt/WO_3 Thin Film by Ti-Doping. *Journal—Ceramic Society Japan*, **123**, 1102-1105. https://doi.org/10.2109/jcersj2.123.1102

[18] Brinker, C.J. and Scherer, G.W. (1990) Sol-Gel Science. Academic Press, Boston.

[19] Deb, S.K. (2008) Opportunities and Challenges in Science and Technology of WO_3 for Electrochromic and Related Applications. *Solar Energy Materials and Solar Cells*, **92**, 245-258. https://doi.org/10.1016/j.solmat.2007.01.026

[20] Pajonk, G.M. (2000) Contribution of Spillover Effects to Heterogeneous Catalysis. *Applied Catalysis*, **202**, 157-169. https://doi.org/10.1016/S0926-860X(00)00522-6

[21] Ohishi, T., Maekawa, S. and Katoh, A. (1992) Synthesis and Properties of Tantalum

Oxide Films Prepared by the Sol-Gel Method Using Photo-Irradiation. *Journal of Non-Crystalline Solids*, **147**-**148**, 493-498. https://doi.org/10.1016/S0022-3093(05)80665-9

[22] Maekawa, S., Okude, K. and Ohishi, T. (1994) Synthesis of SiO$_2$ Thin Films by Sol-Gel Method Using Photoirradiation and Molecular Structure Analysis. *Journal of Sol-Gel Science and Technology*, **2**, 497-501. https://doi.org/10.1007/BF00486297

[23] Ohishi, T., Maekawa, S., Ishikawa, T. and Kamoto, D. (1997) Preparation and Properties of Anti-Reflection/Anti Static Thin Films for Cathode Ray Tubes Prepared by Sol-Gel Method Using Photoirradiation. *Journal of Sol-Gel Science and Technology*, **8**, 511-515. https://doi.org/10.1007/BF02436891

[24] Okusaki, S. and Ohishi, T. (2003) The Effect of Photo-Irradiation in Hydrolysis and Condensation of Silicon Alkoxide. *Journal of Non-Crystalline Solids*, **319**, 311-313. https://doi.org/10.1016/S0022-3093(02)02054-9