Effect of ambient oxygen and temperature on gaschromic properties of Pt/WO_3 thin film exposed by hydrogen

Kenta Yashiki, Tsuneyoshi Matsuoka, Yuji Nakamura
Department of Mechanical Engineering, Toyohashi University of Technology
Toyohashi, Aichi, Japan

1 Introduction

Hydrogen is receiving attention as a promising clean fuel for the near future. Nevertheless, because of its wider explosion range (4 ~ 75 vol. % in air) as well as its lower minimum ignition energy (0.02 mJ), the risk management of its leakage is one of the serious issues to be considered. With respect to this, detection of the leakage is an important task to prevent potential accidents. Generally, hydrogen sensors are based on utilizing the variation of electric characters, for instance, catalytic combustion and thermo-electro conversion types are such examples [1]. However, they are only capable of detecting "local" hydrogen concentration near where the sensor is placed so that the actual concentration profile is hardly known unless a great many sensors are placed everywhere. In addition, they generally need power sources and detectors to work so that a certain volume or electric circuit is necessary. Namely, there is a possibility (low but not zero) that they risk being an ignition source via short-circuiting peripheral devices. Of course, the response delay must be short enough to ensure safety. As summarized above, the preferable features of a hydrogen sensor are that (1) it can be applicable to sense a wide zone at once (not point-sensing, but surface sensing), (2) no power source and electric circuit is required, (3) quick response and easy to detect. Utilizing thin film gas-sensing devices is one of the potential solutions in this regard.

A platinum-supported tungsten oxide (Pt/WO_3) has a gaschromism feature for an adjacent hydrogen gas. Here, "gaschromism" stands for reversible color changing by chemical reaction. Hydrogen molecules are dissociated on Pt catalyst and ionized to protons and electrons. These diffuse toward the WO_3 surface (so called "spillover") and HWO_3 is generated by inserting into the WO_3 structure. Because of the photo-absorption feature of HWO_3 ranging approximately from 500 nm to longer, a blue color appears. These reactions are summarized as follows [2];

$$H_2 \xrightarrow{Pt} 2H \longrightarrow 2H^+ + 2e^- \quad (1)$$

$$H^+ + e^- + WO_3 \longrightarrow HWO_3 \quad (2)$$

Correspondence to: yuji@me.tut.ac.jp

Formed HWO_3 is then oxidized to return to WO_3 via dehydration reaction, which prevents the coloring;

$$2HWO_3 + \frac{1}{2}O_2 \xrightarrow{Pt} 2WO_3 + H_2O \quad (3)$$

At oxygen-existing environment, reactions (2) and (3) occur concurrently and simultaneously to affect the coloring character. Color change of Pt/WO_3 thin film by exposing hydrogen is easily detected by the naked eye and a hydrogen leakage detection system can be simplified accordingly. Unlike existing detection devices, no electric circuit is necessary thereby removing the ignition risk. Moreover, technically the thin film can be placed on any surface so that any surface can act as sensor. The response time would be controlled by the film's character (e.g., thickness), although this needs to be confirmed. The catalytic combustion of hydrogen on Pt surface may cause fire accidents. For example, it is shown that ignition takes place within about 4 minutes when 7.0 vol. % hydrogen-air mixture flows at 0.25 m/s over Passive Autocatalytic Recombiners (REKO-3 type) which are used in nuclear power plant [3]. However, the Pt/WO_3 film proposed in this study will be applied for early-hydrogen detection. The time scale for detection supposed in practical use is much smaller (second order smaller) than that of the catalytic combustion.

Several researches on the gaschromism feature have been performed, although they were somewhat limited. Yamaguchi et al [4] studied the effect of ambient oxygen concentration on the coloring feature of Pt/WO_3 thin film at a fixed (room) temperature. Okazaki et al [5] studied the effect of temperature (233 K to 373 K) on the coloring feature of Pt/WO_3 thin film with using 4.0 vol. % of hydrogen gas diluted by nitrogen under a zero oxidizer environment. As described above, reaction (3) plays an important role on preventing the coloring and all reactions should have strong temperature dependency based on Arrhenius law. In this regard, the effects of temperature and oxygen concentration must be considered simultaneously. In this study, we prepared hand-made Pt/WO_3 thin films and investigated the hydrogen gas sensing performance of Pt/WO_3 in various atmospheric conditions, especially selected combinations of initial temperatures and oxygen concentrations.

2 Experimental method

2.1 Preparation of Pt/WO_3 thin films

Pt/WO_3 thin film was prepared by sol-gel method followed by Yamaguchi et al [4]. Tungsten hexachloride (WCl_6, Kojundo Chemical Laboratory Co., Ltd., 99.99 %) was used as tungsten source, whereas hydrogen hexachloroplatinate (IV) hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, Kanto Chemical Co., Inc., 98.5 %) was used as platinum source. A 9.95 g of WCl_6 was dissolved in 100 mL of ethanol (Kanto Chemical Co., Inc., 99.5 %) and 1.00 g of $H_2PtCl_6 \cdot 6H_2O$ was dissolved in 42 mL of ethanol. They were mixed together in the nitrogen-filled glovebox to prevent any oxidation and be ready to use as a source of the target product (mol ratio of W/Pt is 13/1). A thin (liquid) film of the solution was formed over an alkaline-free glass substrate (Corning Eagle XG) by a spin coating system (MIKASA Opticoat MS-A100). The spin-coatings were made using the following 4 steps, 1: dropped the solution on the glass substrate, 2: rotated the spin-coater at 500 rpm for 10 seconds, 3: dried on a hot plate at 370 K for 30 minutes. 4: repeated 1 ~ 3 processes at predetermined times to have a multi-layered structure (lamination). Eventually the thin (liquid) film shall be subjected to a heat-treated environment in the hot furnace at 720 K for 10 minutes to form a thin film. Three kinds of "layered" films are prepared in this study to check the effect of the number of laminations on coloring characters. Structural characterization of the film was confirmed by Scanning Electron Microscope Energy Dispersive X-ray Spectrometry (SEM-EDX, SU3500, Hitachi High-Technologies)

and X-ray Diffractometer (XRD, RINT-2500, Rigaku) using CuKα radiation (X-ray tube voltage: 40 kV, X-ray tube current: 200 mA), equipped at Research Facility Center, Toyohashi University of Technology. We obtained a cross-sectional image of the film including glass substrate by SEM (SU3500) using 15 kV of accelerating voltage and the film thickness was measured by using image analysis through ImageJ [6].

2.2 Hydrogen exposure test

Detail of the experimental chamber for hydrogen gas sensing performance test is depicted in Figure 1. White LED light was used as a light source. The film was set vertically and a hydrogen nozzle is placed 1 mm away from the surface to expose impinging pure hydrogen jet flow at room temperature onto the surface. Hydrogen flow rate was controlled at 25 cc/min by mass flow controller (SEC-E40, HORIBA). Oxygen concentration and temperature in the chamber was controlled prior to the test and monitored by multi-gas detector (XP-3118, New Cosmos electric Co., Ltd.) and data logger (GL900, Graphtec) during the test. Time-variation of coloring feature of Pt/WO_3 thin film was monitored by digital video camera (Canon iVIS HF G10) from back surface of the film. Experimental conditions are summarized in Table 1.

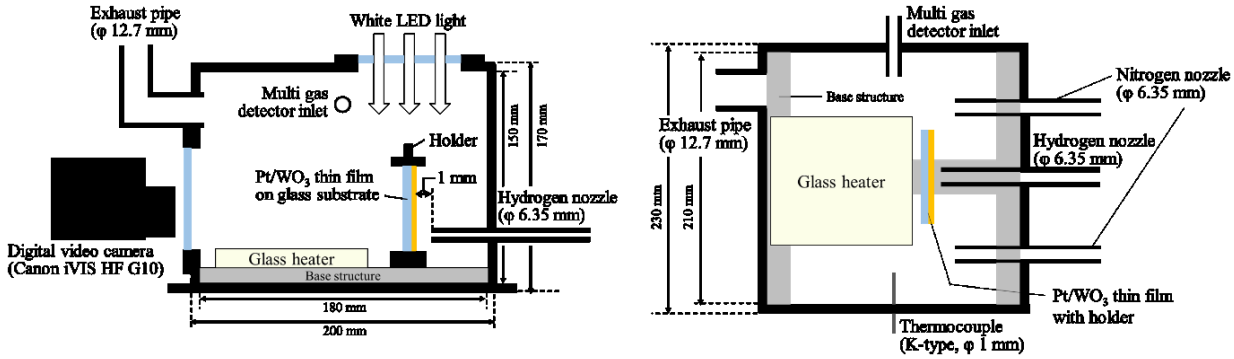

Figure 1. Detail of the experimental chamber for hydrogen gas sensing performance test, left: side view; right: top view

Table 1. Conditions of hydrogen gas sensing performance test

Hydrogen gas flow rate	25 cc/min (37.5 μg/s)
Hydrogen gas concentration	100 %
Number of lamination of Pt/WO_3 thin film	2, 4, 6
Oxygen concentration in the chamber	8, 10, 15, 20 %
Temperature in the chamber	Room, 310 K, 330 K

3 Results and Discussion

3.1 Structure of Pt/WO_3 thin film

The results of SEM-EDX measurement and XRD measurement of the film are shown in Figure 2. Platinum spectrum appeared near 2.0 keV, but tungsten spectrum was not specified because the

characteristic X-ray excitation voltage of tungsten is very near to silicon. The main diffraction peak was confirmed nearly 23 °, 28 °, 34 ° from XRD measurement. Compared to WO_3 spectrum of International Centre for Diffraction Data (ICDD) database [7], this result shows good agreement in all ranges considered in this study. From both results, we confirmed that the produced film is satisfactory to be treated as Pt/WO_3 thin film. Cross-sectional SEM image of the thin film is shown in Figure 3 (left). Two layers, being a Pt/WO_3 layer and a glass substrate layer, were confirmed clearly. The atomic number of tungsten is higher than the silicon used as the glass substrate material, in other words, tungsten has many electrons compare to silicon. Thus, a layer including tungsten looks bright compared to the glass substrate layer in the SEM image. In this way, the thickness of the Pt/WO_3 layer can be specified. The result of film thickness measurement by image analysis is shown in Figure 3 (right). The thickness increased as expected when increasing the number of laminations, suggesting that film thickness can be controlled easily by the number of laminations (film-making process).

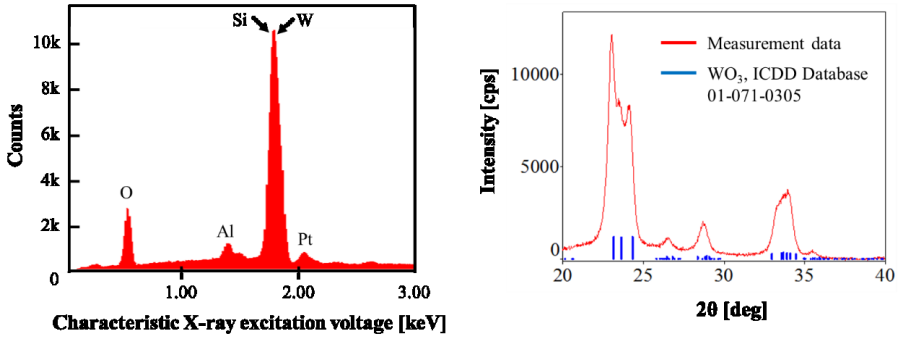

Figure 2. The qualitative analysis of the prepared films, left: EDX analysis (0 ~ 3.00 keV); right: XRD pattern (20 ° < 2θ < 40 °)

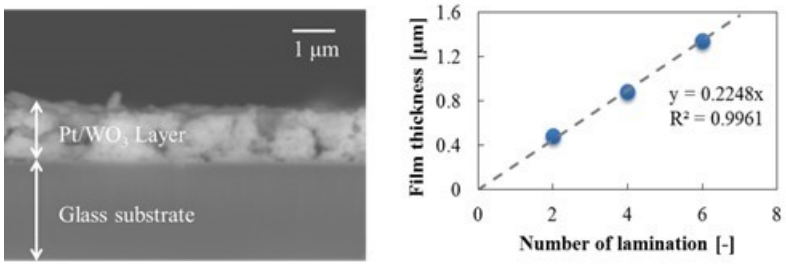

Figure 3. Left: cross-sectional SEM image of Pt/WO_3 thin film (number of lamination: 6); right: the relationship between the number of laminations and film thickness

3.2 Hydrogen exposure test

Figure 4 shows the typical time-variation of coloration of Pt/WO_3 thin film by exposing hydrogen gas. Hydrogen gas exposure is only operated from t = 10 s to 35 s. The film colored blue immediately after exposure, whereas it was bleached by ambient oxygen gradually after the hydrogen gas supply ceased. As clearly found, its color change is visually detectable and the response delay is satisfactorily short. Selected result of the time-variation of normalized intensity changing in various conditions are shown in Figure 5. Note that the data shown here is averaged ones near the hydrogen impinged region. In the figure, the effects of thickness of the film, ambient oxygen and ambient temperature are shown and found that all

factors give a similar impact to the coloration features, implying that they are all competing against each other. It is understood that coloration rate increased as the film thickness increased, suggesting that the thicker film is suitable for the detector under the condition studied in this work (see left of Fig. 5). It is also understood that the coloration rate decreased as ambient oxygen concentration increased, in particular, the change of normalized intensity was small when ambient oxygen concentration is 20 % (see center of Fig. 5). This result suggest that the present system is suitable to apply for the detection of hydrogen under a lower oxygen concentration atmosphere (such as a fire environment, for instance). Lastly, it is confirmed that the coloration rate increased as ambient temperature increased as reported by Okazaki et al [5]. It is interesting to note that the response delay time becomes slower at first under the higher temperature environment.

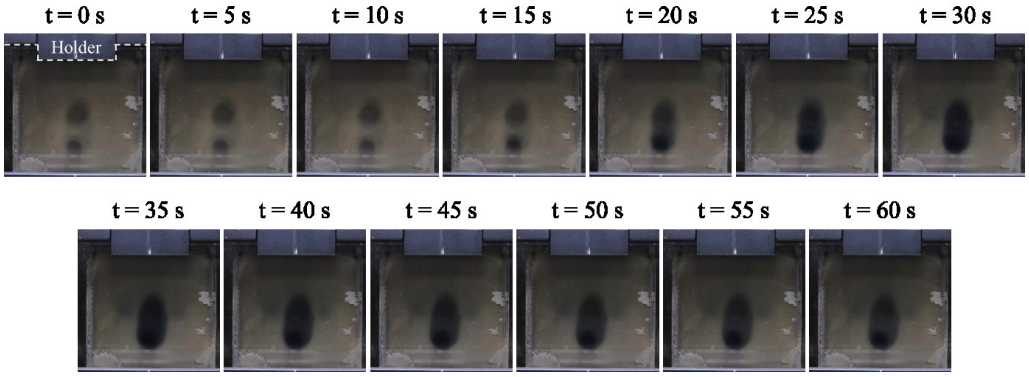

Figure 4. The time histories of coloration of Pt/WO_3 thin film by exposing hydrogen gas (number of lamination: 6, ambient oxygen concentration: 10 %, ambient temperature: 330 K)

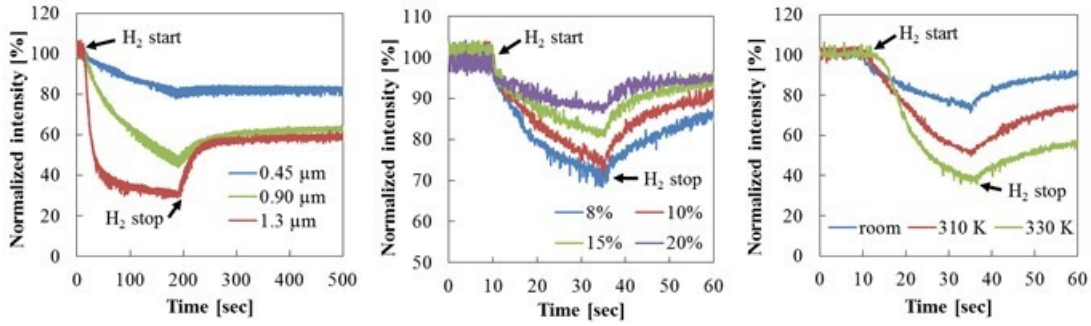

Figure 5. The time histories of normalized intensity of Pt/WO_3 thin films in various conditions, left: changed calculated film thickness (fixed ambient oxygen concentration and ambient temperature in 10 % and 310 K); center: changed ambient oxygen concentration (fixed calculated film thickness and ambient temperature in 1.3 μm and room temperature); right: changed ambient temperature (fixed ambient oxygen concentration and calculated film thickness in 10 % and 1.3 μm)

According to Georg et al [8], the coloration steps of Pt/WO_3 are summarized as follows, 1: adsorption and dissociation of the H_2 on the catalyst, 2: transport of the H atoms to the WO_3 surface, 3: reaction of the H with the WO_3, formation of color centers, 4: diffusion of color centers into the interior of the WO_3. The film thickness affects an increment of surface area so that adsorption site of hydrogen is increased. This attributes to increase the coloration rate accordingly. Effect of ambient temperature is somewhat tricky because it affects not only the reaction rates but also the transport rate. To be more concrete, careful

measurement on temperature dependency would be highly necessary. Currently we are upgrading the experimental system to make this possible.

4 Concluding remarks

In this study, we prepared Pt/WO_3 thin film and investigated the temperature dependence on the hydrogen gas sensing performance of Pt/WO_3 under various oxygen environments. We could establish a satisfactory evaluation system to investigate the capability and performance of the Pt/WO_3 thin film for a hydrogen sensor under various environmental conditions. Existence of Pt and WO_3 are confirmed by SEM-EDX and XRD, and the film thickness linearly increases with the number of laminations. Through the hydrogen detection test, it is found that the thicker film is preferable for an early-hydrogen detection purpose. It is also understood that the film system would work preferably under lower oxygen concentration at higher temperature. It is confirmed that the coloration feature of Pt/WO_3 thin film exposed by the pure hydrogen is affected not only by the film thickness, but also ambient oxygen concentration and ambient temperature. Because all factors show a similar impact to the coloration rate, it is suggested that they would be competing against each other. Further careful study is needed to confirm the precise coloration performance of the Pt/WO_3 thin film.

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