Influence of temperature and humidity on the electrical sensing of Pt/WO_3 thin film hydrogen gas sensor

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Platinum catalyst loaded tungsten oxide (Pt/WO_3) is a promising candidate as a hydrogen gas sensor material, which can detect it through optical and electrical sensing. The sensor, which can detect the hydrogen gas stably in various environments, is strongly demanded. In this study, we prepared the Pt/WO_3 thin film by the sol–gel method and evaluate the dependence of the hydrogen gas sensing property on measuring temperature and humidity. Hydrogen gas sensing property of Pt/WO_3 thin film was evaluated by measuring the electrical conductivity with humid (0–100% of relative humidity) hydrogen gas exposure at various temperatures. The sensing property was declined in humid atmospheres because the water molecule adsorbing on the hydrogen gas sensing of Pt/WO_3 have

1. Introduction

Hydrogen gas attracts much attention as next generation clean energy resource. Particularly, fuel cell using hydrogen is clean and highly efficient. Then, the development of many technologies concerned with the production, transportation, store and use is strongly required. Hydrogen gas has a 3.46 m/s of fast combustion rate, and explodes in wide concentration range under air atmosphere. Thus, hydrogen is dangerous compared with other combustible gases. In addition, it is odorless and transparent, and the most diffusive gas due to the light mass. Therefore, high performance hydrogen gas sensor, which can detect it in wide concentration range immediately, is required. In this study, we focused on a platinum catalyst loaded tungsten trioxide (Pt/WO_3).

WO_3 is widely used as functional ceramic material such as photocatalysis. Particularly, WO_3 is a typical chromic material, which shows the reversible color change from light yellow to blue along with redox. Electrocatalysis of WO_3 occurring by electrochemical redox was discovered by S. K. Deb in 1973.1,2 Pt catalyst loaded WO_3 shows gasochromism by reacting with hydrogen gas. When the protons and electrons are injected into WO_3 lattice by Pt catalyst, these electrons are trapped at W ions sites, and W_2O_5 is reduced to W(OH)_2.3 This leads the inter valence charge transfer and WO_3 absorbs the light at the range from visible to near-infrared.3–5 Then, WO_3 turns to blue color. Besides, the electrical conductivity of the blue-colored WO_3 becomes higher because the injected electrons and protons work as electrical carriers. Therefore, Pt/WO_3 is one of a promising candidate material, which can detect hydrogen gas optically,6–8 and electrically.9–12 Optical absorbance and electrical conductivity changes of Pt/WO_3 sensor were change with the partial pressure of hydrogen gas. From this, it can detect the concentration of hydrogen gas in air. However, these absorbance and conductivity also depend on the oxygen partial pressure.13 Therefore, we had to investigate the equilibrium among hydrogen, oxygen and Pt/VO_3, and revealed the dependence of Pt/WO_3 gasochromism on hydrogen and oxygen gas partial pressure, described as Eq. (1).14

\[
\frac{1}{[\text{H}_2\text{WO}_3]} = \frac{1}{K} \left( \frac{A \text{[Pt]}}{\text{[H]}^4} - 1 \right)
\]

(1)

It was suspected that gasochromism is affected by temperature because it is the equilibrium reaction. Injection of protons and electrons can be described as Eq. (2). These work important roll in a hydrogen detection of Pt/WO_3. In contrast, the elimination of these carriers are occurred by the reaction between oxygen molecule, described as Eq. (3).

\[
\frac{1}{2} \text{H}_2 + \text{WO}_3 \xrightarrow{\text{Pt}} \text{H}_2\text{WO}_3
\]

(2)

\[
\text{H}_2\text{WO}_3 + \frac{\text{O}_2}{4} \xrightarrow{\text{Pt}} \text{WO}_3 + \frac{\text{H}_2\text{O}}{2}
\]

(3)

For using the Pt/WO_3 thin film at low temperature around room temperature, we have to consider not only the influence of oxygen, but also humidity. Some studies about the influence of water molecule on the hydrogen gas sensing of Pt/WO_3 have
been reported. Georg et al. had been report that the water in the film promoted the diffusion of hydrogen and improved the hydrogen gas sensing property.\textsuperscript{13} It was reported that the water vapor also enhances the sensitivity of against the hydrogen with an increase of humidity.\textsuperscript{16} In contrast, there is the report that the optical hydrogen gas sensing property of Pt/WO\textsubscript{3} declined with an increase of humidity.\textsuperscript{17} Therefore, the unified theory concerned with influence of humidity was not established and the further research was required. Particularly, it is considered that humidity dependence was different from other films because the Pt/WO\textsubscript{3} thin films prepared by the sol–gel process in this study. The films are porous and have large surface area compared with films prepared by a physical vapor deposition method such as an RF sputtering.

In this study, we prepared the Pt/WO\textsubscript{3} thin film by the sol–gel process, and evaluated the hydrogen sensing properties of the film in various measurement conditions. Influence of the humidity was evaluated by measuring in various temperatures and relative humidity atmosphere.

2. Experimental

2.1 Sample preparation

Pt catalyst loaded WO\textsubscript{3} thin film was prepared by the sol–gel process using tungsten hexachloride (WCl\textsubscript{6}) and hydrogen hexachloroplatinate (H\textsubscript{3}PtCl\textsubscript{6}·6H\textsubscript{2}O) as starting materials [14, 15, 21]. In the glove box filled with pure nitrogen, 3.00 g of WCl\textsubscript{6} (Kojundo Chemical Laboratory Co., Ltd., 99.99%) and 0.303 g of H\textsubscript{3}PtCl\textsubscript{6}·6H\textsubscript{2}O (Kishida Chemical Co., Ltd., 98.5%) were dissolved to 42 mL of ethanol (Kanto Chemical Laboratory Co., Inc., 99.5%). The molar ratio of Pt/W was 1/13 in this coating solution. This coating solution was spin-coated on the alkaline-free glass substrate (Corning EAGLE XG), and then dried at 100°C for 10 min. After 4 times repetition of the coating, the film was heat-treated at 400°C for 10 min in a furnace.

2.2 Characterization

The crystal phase and crystallinity were confirmed by the X-ray diffractometer (UltimaIV, Rigaku, Japan) using Cu Kα radiation (40 kV, 40 mA). The morphology and thickness of the Pt/WO\textsubscript{3} was observed by field emission scanning electron microscopy (FE-SEM JSM-7600F, JEOL, Japan) using 15 kV of accelerating voltage.

The electrical conductivity was measured in the steel cell filled with various hydrogen gases by the two-wire method using a digital multi-meter (ADCMT 7410E) and a comb-shaped gold electrode was deposited on the film by thermal evaporation.

Figure 1 shows the measurement system. The electrical conductivity was measured in 1% hydrogen gas diluted with synthetic air, achieved by controlling the flow rate of each gas. Mass-flow controllers mixed the hydrogen, pure nitrogen and pure oxygen gases to prepare the experimental hydrogen gases. Humid hydrogen gas was obtained by getting through pure water by bubbling. Humidity of hydrogen gas was controlled by the mixing ratio with humid and dry hydrogen gas. All experiments were measured under atmospheric pressure, and electrical conductivities were measured at 30, 60, 100 and 150°C.

3. Results and discussions

From the XRD pattern of Pt/WO\textsubscript{3} thin film, the diffraction peaks were indexed as orthorhombic WO\textsubscript{3}. In addition, this film was considered to contain the amorphous phase because the diffraction intensity was slightly weak. This is the characteristic points of Pt/WO\textsubscript{3} film, which shows the superior hydrogen gas sensing property.\textsuperscript{13} The film thickness was about 400 nm, observed by cross-sectional SEM images.

Figure 2 shows the electrical conductivity change of Pt/WO\textsubscript{3} film by 1% hydrogen gas exposure with various humidity conditions. The measurement temperature was controlled at 30–150°C. Before the hydrogen gas exposure, electrical conductivity of the film in humid conditions, e.g. R.H. = 78.4 or 95.9%, increased more than 10\textsuperscript{5} times in comparison with that of dry atmosphere, as shown in Fig. 2(a). It was considered that current could pass the adsorbed water layer on the film surface because a large amount of water molecules adsorbed on surfaces of Pt and WO\textsubscript{3} due to high humidity. Besides, the values of electrical conductivity changes in humid conditions were extremely small compared with dry condition. It was 10 times smaller or more. This was because the hydrogen gas adsorption onto Pt surface was disturbed by the adsorbed water molecules. In Fig. 2(b), electrical conductivities were stable in all humidity conditions at 60°C. In addition, the conductivities showed similar responses to hydrogen gas exposure under various humidity conditions. In the case of R.H. = 2.6%, the conductivity showed a large increase by hydrogen. After that, it was observed that the conductivity decreased slowly and then reached to a similar value in other humidity conditions. We have reported that the electrical conductivity change showed the overshoot behavior due to the equilibrium between the hydrogen injection to WO\textsubscript{3} and the elimination by oxygen, in the dry atmosphere.\textsuperscript{13} In the air atmosphere, hydrogen was injected into the lattice WO\textsubscript{3} as states of protons and electrons as shown in Eq. (2). After the hydrogen injection, the elimination of these electrical carriers, protons and electrons, immediately occurred by oxygen, as shown in Eq. (3).

Therefore, the decrease of the conductivity was observed after the large increase by hydrogen gas exposure, when the humidity is small. However, this behavior could not be observed in humid conditions. The conductivity slowly increased and reached to an equilibrium value. It was considered that the reaction between hydrogen gas and Pt was disturbed by the adsorbed water molecule in spite of measuring at 60°C, and a rate of hydrogen supply into WO\textsubscript{3} film was decreased. Thus, the overshoot behavior of the conductivity change was not observed in humid conditions. In the cases of measurements at 100 and 150°C, the electrical conductivities showed similar responses to hydrogen gas in all
humidity conditions, as shown in Figs. 2(c) and 2(d). Thus, the influence of humidity on hydrogen sensing can be ignored at more than 100°C. In this study, the humidity was measured at room temperature before the hydrogen flowing to a sample cell.

Accurately, relative humidity in a sample cell was varied by measurement temperature because the saturated water vapor pressure increased with an increase of temperature. At the high temperature more than 100°C, Pt/WO₃ can detect hydrogen gas stably because the coverage of water molecule on Pt catalyst surface became low due to a low relative humidity at high temperature.

Pt is the typical heterogeneous catalyst, and has the active site only on the surface. It is well known that the activity is lowered by some adsorption species, such as CO and H₂S. This is called as catalytic poison caused by polar molecules. Water is also polar molecule and can adsorb on the Pt surface stably at low temperature.⁶ Then, we focused on the catalytic combustion of hydrogen molecule on Pt surface in order to observe the catalytic reaction between hydrogen and Pt. The combustion of hydrogen is also occurred on Pt after a hydrogen adsorption. Hydrogen molecule is dissociated to hydrogen atoms after the adsorption. These hydrogen atoms react with oxygen or WO₃. Therefore, the combustion and gasochromic reaction are occurred at the same time. This catalytic combustion can be observed by measuring the surface temperature of Pt/WO₃ film. If the Pt surface was completely covered with water molecule, it is considered that the hydrogen combustion will be disturbed because the hydrogen adsorption will be disturbed. Therefore, it is considered that the interaction between Pt catalyst and water molecule can be observed by measuring the surface temperature change by hydrogen gas exposure in various humidity conditions. Figure 3 shows the temperature change of Pt/WO₃ surface by 1% of hydrogen gas exposure in various humidity conditions at 30, 60 and 100°C. These temperature changes were measured by a thermocouple placed on the film surface in same system as shown in Fig. 1.

In case of measuring at 30°C, as shown in Fig. 3(a), surface temperature increased with an increase of temperature. At the high temperature more than 100°C, Pt/WO₃ can detect hydrogen gas stably because the coverage of water molecule on Pt catalyst surface became low due to a low relative humidity at high temperature.

In Fig. 4, Δσ was plotted as a function of relative humidity. Δσ is change value of electrical conductivity before and after of hydrogen gas exposure. It was found that the film shows the about 10⁻⁴ S cm⁻¹ of electrical conductivity change for 1% hydrogen gas exposure in all measurement conditions between 30°C.
and 150°C. It was considered that these change values were relatively large because the conductivity of the first state is $\approx 10^{-8}$. In the temperature range between 60 and 150°C, the conductivity hardly showed large changes with the increase of humidity. In contrast, the conductivity decreased with increasing the humidity at 30°C, as shown in Fig. 4. Relative humidity can be described as Eq. (4) using the saturated water vapor pressure ($p^s$) and partial pressure ($p$) of water.

$$\text{R.H.} (%) = \frac{p_{H_2O}}{p^s_{H_2O}} \times 100$$

Fig. 3. Surface temperature changes of Pt/WO$_3$ films by 1% hydrogen gas exposure with various humidity conditions at (a) 30°C, (b) 60°C and (c) 100°C.

Fig. 4. Electrical conductivity change values of the film by 1% hydrogen gas exposure under the various relative humidity atmospheres, measured at various temperatures.

For example, when the R.H. was 90% at 30°C, it can be decreased to 19% by heating up to 60°C. Particularly, it decreases to 4% at 100°C. Therefore, it was found that the Pt/WO$_3$ thin film can detect the hydrogen gas immediately removing the influence of humidity by heating around 60°C. As above-mentioned, although the conductivity change value at 60°C was stable, it took a time to reach the equilibrium value because the response to hydrogen gas was slightly slow. In order to remove the influence by adsorbed water, the heating to 100°C is required.

4. Conclusion

In this study, humidity and temperature dependence of hydrogen gas sensing properties of Pt/WO$_3$ thin film was evaluated. The film was prepared by the sol-gel process. In the dry atmosphere, the electrical conductivity of the film was increased immediately by hydrogen gas exposure at all temperature conditions. However, hydrogen gas sensing property was declined with an increase of humidity, at room temperature. When we observed the catalytic combustion of hydrogen gas on Pt by measuring the surface temperature elevation, the catalytic combustion was also disturbed in humid hydrogen gas at room temperature. Thus, it was considered that the adsorbing water molecule on the Pt surface mainly disturbed a reaction between hydrogen and Pt, and it declined the sensor response. The sensor response can be improved by heating the film at more than 60°C, in any humid conditions. The water molecule can be easily removed from Pt because the saturated water vapor pressure increases and the relative humidity decreases rapidly at high temperature more than 60°C.

References