DOI 10.5162/IMCS2012/8.5.2

Anomalous Gasochromic Response Behavior in Hydrogen Sensing with Pt/WO_3 Film at Low Temperature Range

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Abstract

Gasochromic characteristics of sol-gel derived Pt/WO_3 film as a hydrogen sensitive material was evaluated at various temperatures in the near-infrared region by optical transmittance measurements. The sensitivity of the film was high and more than 60% transmittance change was observed at room temperature and higher, with 4 % H_2/N_2 balance gas. The curves may be approximated by exponential response. The response speed was fast and the 63% response time was about 5 sec. at 25 °C. On the other hand, recovery speed was slower than that of the response, suggesting that the recovery process may not be a reverse reaction of the response mechanism. As temperature lowers, the response becomes slower and weaker, yet reasonable response was still observed at 0 °C. However, anomalous response behavior was observed at -40 °C. The behavior may be attributed to the effect of water formed by the recovery reaction.

Key words: Gasochromism, Hydrogen leak detection, Platinum-supported tungsten trioxide, Response kinetics, Long-term stability

Introduction

A clean energy system using hydrogen has been attracting much attention as a solution against global warming problem. However, hydrogen has explosive nature, and the leakage detection of hydrogen gas is very important. Many sensor devices have been proposed and practically used. Among them optical methods such as fiber-optic gas sensors have the advantages of explosion-proof and immunity to electromagnetic noises. The Pt/WO_3 thin film is frequently utilized as sensing material in this type of sensors. The gasochromic coloring reaction readily proceeds when the film is exposed to hydrogen gas [1]. However, it has been reported that reaction rate was influenced by various environmental factors [2,3]. Considering practical application in harsh environments such as cold area, quantitative evaluation of sensor performance at low temperature range is crucial and suitable technical countermeasures should be developed if necessary. In this study, temperature dependence of gasochromic properties and its stability was intensively studied.

Sensing principle

In the presence of hydrogen gas, hydrogen molecule dissociates on the Pt catalysts into hydrogen atoms. They spill over and react with tungsten trioxide to form blue tungsten bronze (H_xWO_3) as coloring reaction. Therefore, optical power transmitted through the Pt / WO_3 thin film attenuates in hydrogen containing atmosphere. In the oxidizing atmosphere, regeneration of WO_3 accompanies bleaching.

Experimental setup

The Pt/WO_3 film was deposited on the quartz glass substrate by the sol-gel method [4]. The sodium tungstate aqueous solution (0.5 M) was passed through cation exchange resin (Amberlite™ IR120B) in hydrogen form. A 6.5 ml of the obtained colloidal tungstic acid solution was mixed with 10 ml of the ethanol/water solution 80 %(v/v) containing 0.09 M hexachloroplatinic acid as catalyst precursor and stirred for 60 sec. This casting solution was spin-coated on the substrate at 500 rpm for 5 min. The coating was dried at room temperature and annealed at 500 °C for 1 h in air condition.

The test sample was placed in an airtight gas chamber which has collimator lenses for transmittance measurements, as shown in Fig. 1. These lenses were connected to near infrared LD light source (1.3 μm, Anritsu co., MG9001A) and optical power meter with InGaAs photodetector (Ando electric co., ltd., AQ2150A) through transmission multimode

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optical fiber cable. H_2/N_2 balance gas (4 vol.%) was used for hydrogen detection and dry air (dew point <-50 °C) from a bottle was flowed for recovery process. All experiments were conducted in temperature-controlled reservoir.

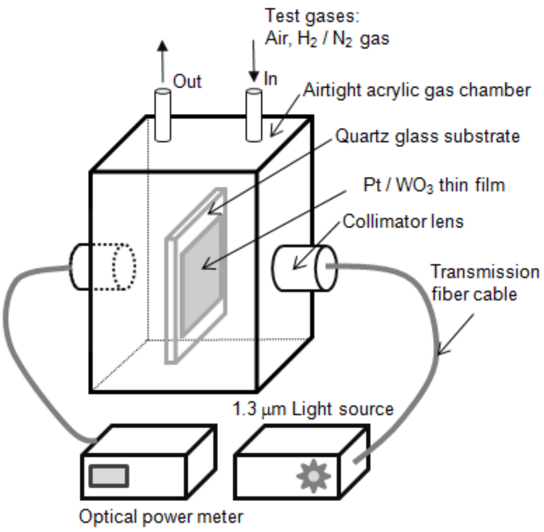

Fig. 1. Experimental-setup for evaluation of gasochromic behaviors of Pt / WO_3 thin film.

Results and discussion

Fig. 2 shows typical gasochromic responses to hydrogen gas at different ambient temperatures. The ordinate of the figure represents normalized optical power with respect to the steady-state transmitted power in air atmosphere at corresponding temperatures. The transmittance of the sample was high (ca. 85%) since the Pt/WO_3 film was semitransparent in air condition. On the other hand, the transmitted power sharply decreased to less than 40% when the film was exposed to 4 vol.% H_2/N_2 balance gas at 25 °C. This coloration resulted from the high optical absorption coefficient of H_xWO_3 formed by hydrogen reduction. Although the data was not shown, almost same transmittance changes with the exposure to hydrogen gas (i.e. sensitivities) were obtained at higher temperature. It is suggested that the formation of H_xWO_3 would saturate at high temperature region. On the other hand, the response becomes slower and weaker as temperature lowers. However, reasonable response was still observed at 0 °C. By replacing hydrogen containing atmosphere to dry air, the recovery (bleaching) reaction proceeded. Although the transmitted power immediately started to increase, the recovery speed was much slower than that of response. It took more than 100 sec. until the sensor signal recovered to baseline at 25 °C.

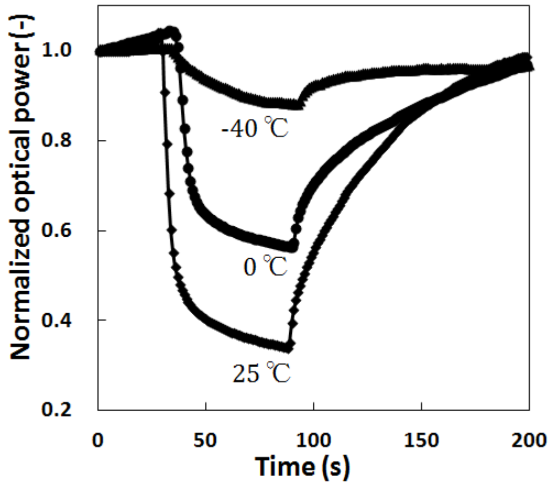

Fig. 2. Typical responses to 4 vol.% H_2/ N_2 at different ambient temperature.

The relationships of the logarithm of normalized response ($R_F(t)$) defined by eq. (1) and time were almost linear (Fig. 3). It indicates that the sensor shows a simple exponential response. The response speed at 25 and 0 °C were fast and the 63% response-times were 5 and 6 sec, respectively.

$$R_F(t) = (P(t) – Ps) / (Pi – Ps) \quad (1)$$

where $P(t)$: measured optical power, Pi : initial optical power, and Ps : saturated value of optical power after hydrogen exposure.

The response at -40 °C became sluggish and the value of the time-constant was about five times larger than that at 25 °C.

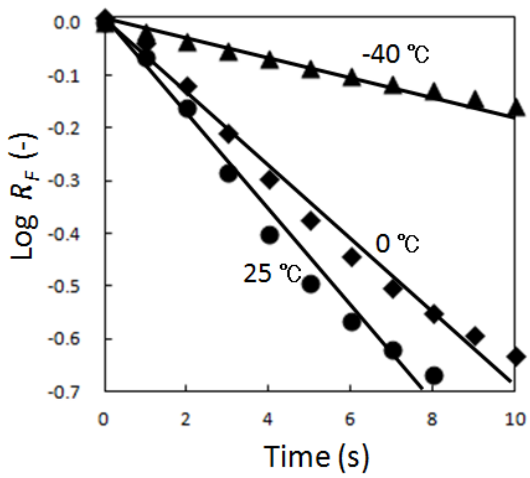

Fig. 3. Relationships between log R_F and time at different temperature.

Similarly, the normalized response for recovery reaction was defined by eq. (2).

$$R_B(t) = (Pi – P(t)) / (Pi – Ps) \quad (2)$$

Fig. 4 shows that nearly exponential response was observed in the initial stage (up to 25 sec). However, the behavior started to deviate from this relation and tended to saturate. The 63% recovery-time was about 40 sec.

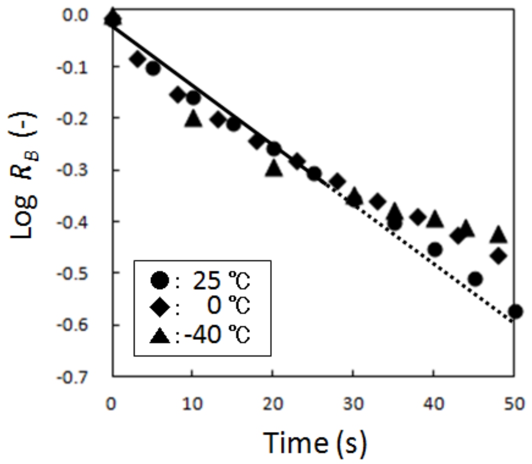

Fig. 4. Relationships between log R_B and time at different temperature.

Furthermore, sensing performance became anomalous with repeated exposures to hydrogen gas and air in below freezing temperature (Fig. 5). It is noted that the spike-like response to air was instantaneously going to opposite direction. Although normal recovery reaction subsequently began, the optical power did not reach to its initial level. Almost same baseline shift was also accumulated at the second response curve. It is indicated that the water, formed by the recovery reaction, froze and stayed in the film. Then tiny and numerous frost particles would scattered the transmitting light.

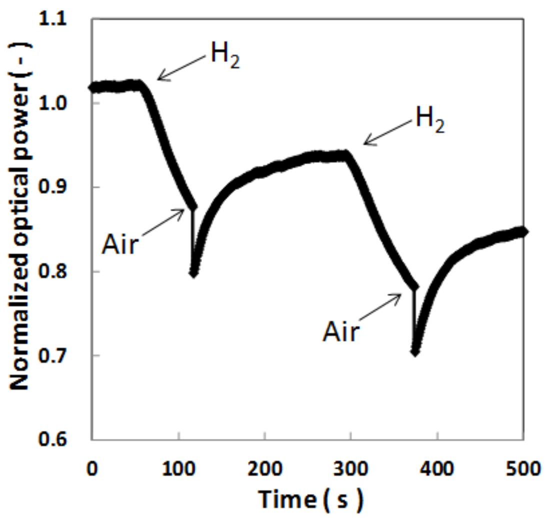

Fig. 5. Anomalous response characteristics at -40 °C.

Conclusion

The coloring and bleaching characteristics at temperature range from -40 to +25 °C were investigated for sensor application in cold environments. The Pt/WO_3 thin film was immobilized on quartz glass substrate as optical hydrogen sensing material through sol-gel method base on ion-exchange process. This film showed good gasochromic response even at low temperature range. The sensitivity and response speed strongly depended on ambient temperature. Therefore, the temperature compensation would be required for reliable leak detection. The anomalous sensing behavior such as spike-like response and discontinuous baseline drift was appeared when the sensor was repeatedly exposed to hydrogen in subfreezing conditions. It would result from accumulation of water or frost formed by bleaching reaction. Application of minimal heating or protective coating in order to eliminate those undesired influences is under investigation.

Acknowledgements

This research was supported by KAKENHI (21560442).

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