

Pt/Pd/WO₃ deposited by reactive sputtering for hydrogen sensor

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Recently interest in alternative energy sources has increased throughout the world due to high oil price and environmental issues. Among alternative energy sources, hydrogen energy has been come into the spotlight in that it is sustainable and ideally pollution-free. In spite of its advantage as an alternative energy source, there are still some technological hurdles that should be overcome before hydrogen can be widely used. In particular, it is necessary to develop hydrogen sensing technology for safe hydrogen utilization. Optical hydrogen safety sensor based on gasochromic thin films, which is one of various hydrogen sensors, can detect the change of color of the film upon exposure to hydrogen gas in an area where hydrogen leak is suspected. For this application, sensitivity and durability of the sensor material is the most important factor.

In this study, we have used Pt/Pd as a catalyst of the hydrogen sensor films. We found that it has improved sensitivity and durability over the usual Pd catalyst.

Keywords: hydrogen sensor, tungsten oxide, sputtering, palladium, platinum, optical

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1. INTRODUCTION

Recent high oil prices and serious environmental problems for fossil energy have rekindled worldwide interests in new alternative energy sources. In particular, hydrogen energy has been watched by the entire world with keen interest due to its renewability and cleanliness as an energy source among variable alternative energy sources. However, it also has high risk of exploding in air.^[1] Therefore it is important to develop the hydrogen sensing technology

in order to bring about the hydrogen economy.

In spite of the fact that both the academia and the industry have researched various types of hydrogen sensor, no clearly superior technology of hydrogen sensors has emerged. Optical hydrogen safety sensors, which detects hydrogen optically unlike many types of existing hydrogen sensors that measure electrically, was introduced.^[2]

This hydrogen optical safety sensor is based on gasochromism, a phenomenon where a material changes color when exposed to a specific gas. In an optical sensor, hydrogen can be remotely detected if

the sensing material and the sensor circuit are connected via an optical fiber. This also eliminates the possibility of ignition of hydrogen explosion due to electrical discharge.

Optical hydrogen sensor films are composed of an electrochromic layer such as tungsten oxide (WO_3) deposited by reactive sputtering and a catalyst layer of Pd. When exposed to hydrogen gas, the catalyst layer of Pd not only decomposed hydrogen gas into electrons and protons, but also diffused these particles into the WO_3 electrochromic layer. Then, electrons reduce W^{6+} ions in WO_3 to W^{5+} ions, and hopping between W^{6+} and W^{5+} in small-polaron transitions cause a color change.^[3] Then, by measuring the optical transmittance or the reflectance of the sensor thin film, the existence of hydrogen can be detected. In this type of a sensor, it is important to improve the ability of the catalyst to decompose hydrogen molecules into electron and proton and diffused them into the electrochromic layer.^[4]

2. EXPERIMENT

Pt/Pd/a- WO_3 thin films were produced by RF & DC Sputtering. The substrates used were glass for monitoring color changes of hydrogen sensor thin films when exposed to hydrogen gas. Amorphous tungsten oxide (a- WO_3) thin films were deposited by sputtering a tungsten target with 99.99% of purity by RF sputtering in Ar and O_2 gas flow.

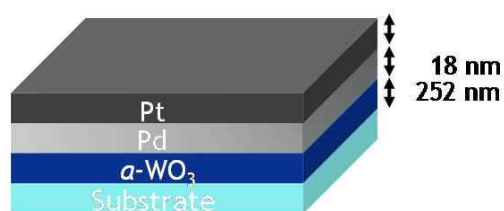


Fig. 1. The structure of a Pt/Pd/a- WO_3 layer. WO_3 252 nm, Pd 18 nm, Pt layer a.; 0, 18, 36 nm

A Pd layer was deposited on top of a- WO_3 by DC sputtering in Ar gas flow. Then Pt layer was coated on top of Pd/a- WO_3 by RF sputtering. The thicknesses of Pd and a- WO_3 layers were 18 nm and 252 nm, respectively. Three samples with Pt-layer thicknesses of 0, 18, and 36 nm were compared.

In order to measure the optical transmittance of Pt/Pd/a- WO_3 when exposed to hydrogen gas, 633nm He-Ne semiconductor laser light was divided into two by a beam splitter. One of the two light beams separated was used as a reference signal, and the other was used as a sensing signal. The sensing signal was injected into hydrogen sensor films inside a chamber through an optical cable. Then we detected the changes in the ratio between the sensing signal and reference signal measured by photodiodes while injecting hydrogen gas and air alternately. The air used in this study was a mixture of 80% nitrogen and 20% oxygen. For hydrogen, 1% concentration of hydrogen gas mixed in the artificial air was used.

In addition, we made a hydrogen optical sensor based on gasochromic thin films developed in this work. It demonstrated fast sensing and long-term durability.

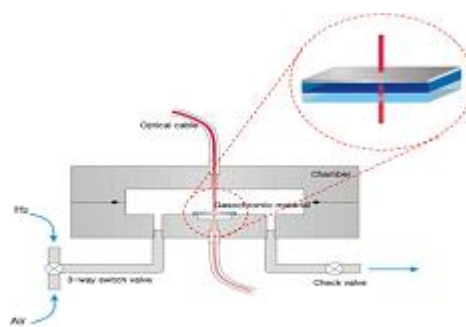


Fig. 2. The optical testing setup for monitoring the optical transmittance of Pt/Pd/a- WO_3 .

3. RESULTS AND DISCUSSION

In order to compare the optical changes of Pd/a-WO₃ with that of Pt/Pd/a-WO₃ when exposed to hydrogen gas, we injected 1% hydrogen gas for 30 second and artificial air for 30 second alternately into the test chamber. Then we found that the thicker Pt layer on top of Pd/a-WO₃, the larger the optical transmittance changes of hydrogen sensor thin films when exposed to hydrogen gas. In case of Pd/a-WO₃, when hydrogen was injected, the optical transmittance decreased by about 25%. However, the change in the optical transmittance in the case of 5Å-Pt/Pd/a-WO₃ was 35%, and that of 10Å-Pt/Pd/a-WO₃ was 50%. It shows that more Pt helps decompose hydrogen molecules. Since Pt is a more effective catalyst than Pd, adding a layer of Pt improves the sensitivity of the hydrogen sensing material.

Fig. 4 is a diagram of a hydrogen sensor based on Pt/Pd/a-WO₃ thin films and a photograph of a hydrogen optical sensor prototype.

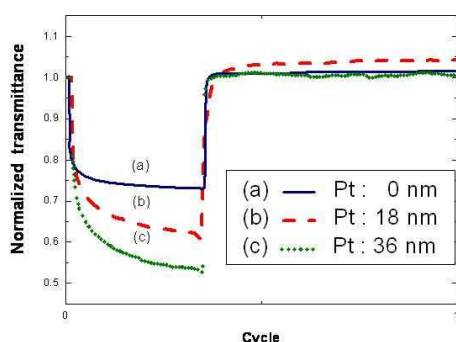


Fig. 3. The optical transmittance change of Pt/Pd/a-WO₃ exposed to 1% hydrogen for Pt layer thickness of (a) 0, (b) 18, and (c) 36 nm.

The light from a He-Ne semiconductor laser, which is separated into two by a beam splitter, enters an optical cable through a beam splitter. The light beam that reaches Pt/Pd/a-WO₃ thin film through optical cable

is reflected by aluminum layer. Then the reflected light enters back into the optical cable.

When exposed to hydrogen gas, a color change of Pt/Pd/a-WO₃ thin film occurred due to its gasochromic property and it caused a decrease of the light intensity reflected.

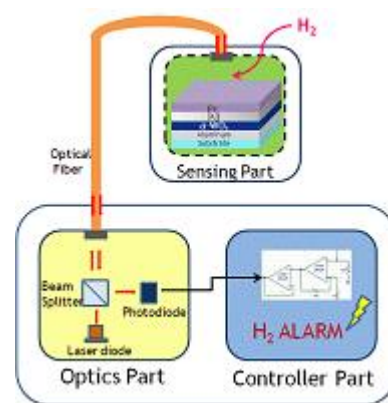


Fig. 4. (a) Structure of hydrogen optical sensor (b) The photograph of hydrogen optical sensor

The other of the separated light beams is used as a reference signal. Then the photodiodes detect these signals and the ratio is calculated by a comparator circuit. When the measured reflectivity falls below a set level, the control circuit sets off an alarm. The best feature of this hydrogen sensor is a fast reaction time of less than 1 second and isolation from electric noise even when the sensing was done over a long distance.

4. CONCLUSION

In this study, we deposited Pt/Pd/a-WO₃ thin films for hydrogen sensor by sputtering. Due to the stronger catalyst performance of Pt, improved sensitivity was achieved. A prototype sensor based on the thin film shows fast and reliable performance.

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