Asian Journal of Chemistry; Vol. 26, No. 17 (2014), 5717-5719

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.18191

Design of Optical Fiber Hydrogen Sensor Based on Platinum-Doped Tungsten Trioxide Films†

ZELUN LI[1,2], CHUANDE ZHOU[2], XIANLING DENG[2,*] and YIKE TANG[1]

[1]College of Mechanial Engineering, Chongqing University, Chongqing 400044, P.R. China
[2]College of Mechanical and Dynamic Engineering, Chongqing University of Science and Technology, Chongqing 401331, P.R. China

*Corresponding author: Fax: +86 23 65023718; Tel: +86 23 65005216; E-mail: instru@163.com

AJC-15779

Tungsten oxide (WO_3) is applied extensively because of its electrochromic, photochromic and gasochromic properties. In this work, a type of optical fiber hydrogen (H_2) sensor based on platinum-doped WO_3 films was designed. The preparation and hydrogen sensing properties of platinum-doped WO_3 films was discussed. The structure of the optical fiber hydrogen sensor was designed and the working principle was analyzed theoretically. The response to hydrogen of the sensor was tested. The results indicate that the optical fiber sensor possesses good sensitivity to hydrogen.

Keywords: Optical fiber sensor, Tungsten oxide films, Optical properties, Hydrogen sensitivity.

INTRODUCTION

Hydrogen has attracted wide attentions in the past several decades due to its significant superiority to traditional fuels in propellant. Both solid and liquid hydrogen are volatile, inflammable and explosive. Hydrogen leaked in air to the concentration threshold will become flammable and explosive under room temperature and standard atmospheric pressure. Therefore, it is of great significance to develop a real-time hydrogen sensor[1, 2]. The traditional hydrogen sensors based on the working principle of electrical characteristics have been developed and applied in some fields[3, 4]. However, some unique fields require a stable and reliable hydrogen sensor as hydrogen is often generated in the space between components and needs long-term continuous monitoring. These couldn't be satisfied by the traditional hydrogen sensors[5,6]. With small size, lighter weight, better electrical insurability, higher sensitivity, wider bandwidth, larger dynamic range and anti-electromagnetic interference, optical fiber hydrogen sensors is superior to the traditional hydrogen sensors and attracts wide attentions all over the world[7,8].

Existing typical optical fiber hydrogen sensors includes interferometric hydrogen sensor, micro-lens hydrogen sensor, evanescent wave hydrogen sensor, fiber Bragg grating (FBG) hydrogen sensor and surface plasmon resonance (SPR) hydrogen sensor. The interfermetric optical fiber hydrogen sensor, proposed by Butler in 1984, is based on a Mach-Zehnder interferometer. Although it is advantageous in detection accuracy, it has a complicated structure and instable single use[9]. The micro-lens optical fiber hydrogen sensor, proposed by Butler in 1991, coats a layer of hydrogen sensitive Palladium films or other palladium alloy films on the fiber end face[10]. Although micro-lens optical fiber hydrogen sensor is cost effective and easy to use due to the simple structure and manufacturing process, it has some disadvantages, such as limited application in point measurement, limited reusability and mutual interference between sensitivity and response time. The evanescent wave hydrogen sensor detects the hydrogen concentration variation according to the relationship between the losses of optical waveguide mode and the refractive index. The evanescent wave hydrogen sensor has high sensitivity, but slow response. Sekimoto *et al.*[11] used two cladding modes of optical fiber to change the intensity of evanescent field. Villatoro *et al.*[12] developed a Pd-plating single-mode conical optical fiber sensor based on the variation of evanescent wave absorption. Yan and Liu[13] researched an optical fiber hydrogen sensor based on evanescent field of Pd films. Since hydrogen will produce additional Bragg wavelength drift when reaches the sensing FBG coated with a layer of Pd films, FBG hydrogen sensor detects the hydrogen concentration variation by analyzing wavelength of reflected lights. With poor resistance to temperature and mechanical stress influence, FBG hydrogen

†Presented at 2014 Global Conference on Polymer and Composite Materials (PCM2014) held on 27-29 May 2014, Ningbo, P.R. China

sensor has to eliminate influencing factors of Bragg wavelength by using corresponding approaches. Sutapun *et al.*[14] Boonsong made a hydrogen sensor with Pd-coated FBG. Peng *et al.*[15] studied the performance of a FBG hydrogen sensor with Pd electroplating and Pd tube cover. SPR optical fiber sensor detects gas concentration variation through the surface plasmon resonance generated by metal films or metal alloy films. Bevenot *et al.*[16] developed a SPR hydrogen sensor based on intensity modulation, which can detect hydrogen concentration from 0.8-100 % quickly. Lin *et al.*[17] designed a Pd-coated metal diffraction grating SPR hydrogen sensor based on angle modulation, which can detect 0.001 % hydrogen concentration theoretically under the optimum condition. Coated with silver films, silicon dioxide films and Pd films, Perrotton *et al.*[18] designed a SPR hydrogen sensor based on wavelength modulation.

As a type of the novel semiconductor materials, tungsten oxide is applied extensively for its electrochromic property. It has been widely used in many different applications, such as electrochromic windows, optical devices, fuel cells, photocatalyst materials and gas sensors, *etc*.[19,20]. In this work, we designed a type of optical fiber hydrogen sensor based on platinum-doped WO_3 films.

EXPERIMENTAL

Preparation of hydrogen sensitive films: In the experiments of preparation hydrogen sensitive films for the optical fiber sensor, tungsten trioxide was used as the basic materials and the platinum-doped WO_3 films were prepared with sol-gel method and magnetron sputtering method (Fig. 1). The major instruments include the analytical balance, WGZ-9073BC-1 electrothermal drying oven, KQ-Q-100DE ultrasound purifier, centrifugal machine, Aquapro water purifier, the constant temperature water bath, Haier refrigerator, KW-4A spin coater, JGP-450 magnetron sputtering equipment and L13130 hydrogen furnace and the major reagent include the following materials: tungsten powder (99.8 %), hydrogen peroxide (30 %), anhydrous alcohol, acetone and platinum (99.95 %).

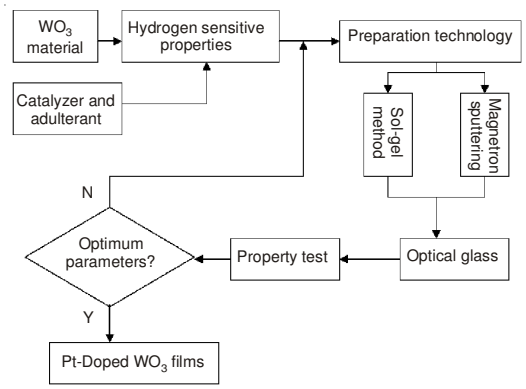

Fig. 1. Preparation of platinum-doped WO_3 films

Design of the optical fiber sensor: The optical fiber hydrogen sensor is designed the probe of the optical fiber sensor (Figs. 2 and 3). The working principle of the optical fiber hydrogen sensor is that the optical properties of platinum-doped WO_3 films will change after absorbing hydrogen. So we can determine the hydrogen concentration by detecting the changes of the optical properties of the films.

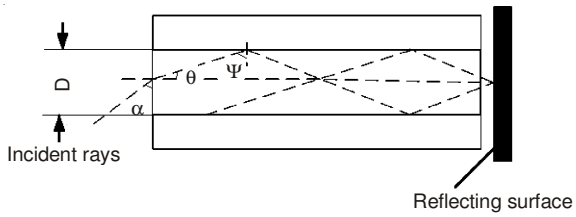

Fig. 2. Structure of the optical fiber hydrogen sensor

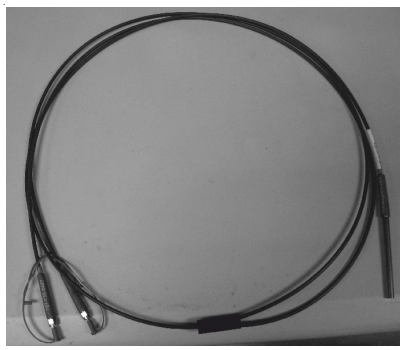

Fig. 3. Probe of the optical fiber sensor

In Fig. 2, platinum-doped WO_3 films were coated on the reflecting surface. Transmission and reflection of the incident light occur simultaneously on the films. Reflected lights are accepted by the optical fiber directly, while some transmission lights will be reflected and transmitted again on the platinum-doped WO_3 films. In the optical model, incident lights in the optical fiber will experience multiple reflections and transmission on the surface of hydrogen sensitive films. As a result, the optical fiber will accept the light intensity reflected directly by the platinum-doped WO_3 films and the light intensity transmitted on the films.

Reflectivity of the incident light on the platinum-doped WO_3 films can be expressed as:

$$R = \left| \frac{r_1 + r_2 \exp(-i\varphi)}{1 + r_1 r_2 \exp(-i\varphi)} \right|^2 \quad (1)$$

where r_1 and r_2 is the Fresnel reflection coefficient, φ is phase shift in platinum-doped WO_3 films.

Suppose the hydrogen sensor gets the input light intensity (I_0) on the platinum-doped WO_3 films, then the light intensity accepted by the optical fiber (I) is proportional to the reflectivity (R(ρ %)) of detected hydrogen concentration (ρ) on the platinum-doped WO_3 films. The detected light intensity after n reflections and refractions can be expressed as:

$$I(\rho\ \%) = I_0 R(\rho\ \%) = I_0 R_1(\rho\ \%)$$

$$+ I_0 (1 - R_1(\rho\ \%))^2 R_2(\rho\ \%) \sum_{n=1}^{\infty} (R_1 R_2)^{n-1} \quad (2)$$

Then, the total light intensity received by the optical fiber (I(ρ %)) can be calculated.

RESULTS AND DISCUSSION

After the hydrogen sensitive films were prepared, the optical and hydrogen sensitive properties of the films were tested. The results show that the hydrogen sensitive properties of the platinum-doped WO_3 films is improved compared with

the WO_3 films without platinum and the sensitivity and reproducibility of the films is satisfactory in the hydrogen concentration range of 80-40000 ppm. Fig. 4 shows the transmissivity of the platinum-doped WO_3 films in different concentrations of hydrogen.

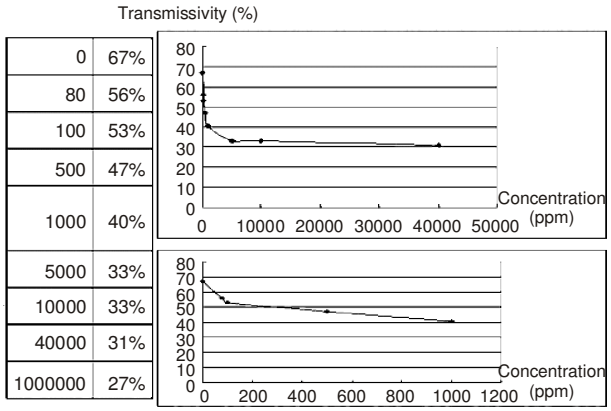

Fig. 4. Transmissivity of platinum-doped WO_3 films

Moreover, we have tested the responses of the films to hydrogen at room temperature when the hydrogen concentration was 4 %. By taking nitrogen gas as zero gas and hydrogen as standard gas and then inputted them into distribution instrument, set the required concentration and turn on the air pump and start to distribute gas. Fig. 5 shows the spectrum of the light intensity change in 4 % hydrogen gas with the optical fiber hydrogen sensor. It can be seen from the figure that the reflected light intensity of the films changed after passing into hydrogen gas and with time increases, the light intensity decreased more and more, but after 10 min, the adsorption of hydrogen gas reached balance and the reflected light intensity was no longer changed.

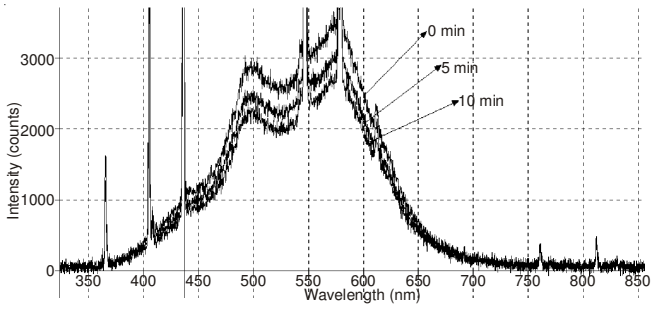

Fig. 5. Light intensity spectra in 4 % H_2 as time increases

At the atmosphere of 4 % H_2, the light intensity change of the samples was about 15 %, taken out the sample after stopping passing into hydrogen and at this time, the colour of the sample was dark blue and then it faded fast after sufficient contact with oxygen in the air. Then we measured the light intensity spectrum and the test results shown in Fig. 6. The figure showed that the light intensity spectra of the films came back to the initial state within 15 min, which suggested that the films possessed good restorative property at room temperature.

Conclusion

A type of optical fiber hydrogen sensor based on platinum-doped WO_3 films was designed in this work. The preparation

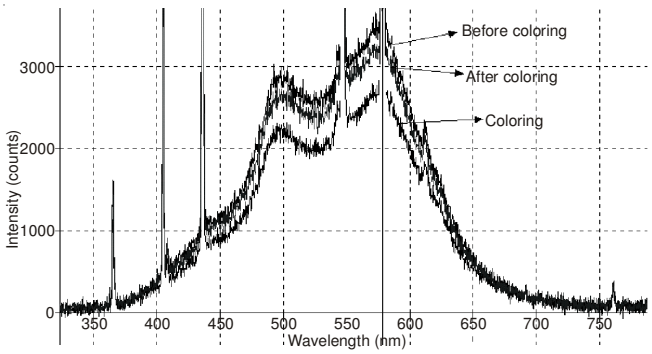

Fig. 6. Light intensity spectra in 4 % H_2 before colouring and after colouring

method of the films was discussed. It is found that the optical properties of the films varies with different hydrogen concentrations, so the hydrogen concentration can be easily detected when the platinum-doped WO_3 films are adopted for the sensor. The structure of the optical fiber hydrogen sensor was designed and the working principle was analyzed. The test results show that the optical fiber sensor possesses good sensitive to hydrogen.

ACKNOWLEDGEMENTS

This work is finically supported by the Project of National Science Foundation of China, NSAF (Grant No. 11076030), the Project of Postdoctoral Science Foundation of China (Grant No. 2012M511901) and the Project of Postdoctoral Science Special Foundation of Chongqing (Grant No. XM20120053).

REFERENCES

1. X. Bevenot, A. Trouillet, C. Veillas, H. Gagnaire and M. Clément, *Sens. Actuators B*, **67**, 57 (2000).
2. J. Villatoro, A. Diez, J. Cruz and M.V. Andrés, *Electron. Lett.*, **37**, 1011 (2001).
3. S. Sumida, S. Okazaki, S. Asakura, H. Nakagawa, H. Murayama and T. Hasegawa, *Sens. Actuators B*, **108**, 508 (2005).
4. K. Schroeder, W. Ecke and R. Willsch, *Opt. Lasers Eng.*, **47**, 1018 (2009).
5. J.B. Beusink, A.M.C. Lokate, G.A.J. Besselink, G.J.M. Pruijn and R.B.M. Schasfoort, *Biosens. Bioelectron.*, **23**, 839 (2008).
6. Y. Jin and Y. Cho, *Trans. Korean Inst. Elect. Eng.*, **58**, 147 (2009).
7. S. Okazaki, H. Nakagawa, S. Asakura, Y. Tomiuchi, N. Tsuji, H. Murayama and M. Washiya, *Sens. Actuators B*, **93**, 142 (2003).
8. M. Stankova, X. Vilanova, J. Calderer, E. Llobet, J. Brezmes, I. Gràcia, C. Cané and X. Correig, *Sens. Actuators B*, **113**, 241 (2006).
9. M. Butler and D. Ginley, *J. Appl. Phys.*, **64**, 3706 (1988).
10. M. Butler, *Sens. Actuators B*, **22**, 155 (1994).
11. S. Sekimoto, H. Nakagawa, S. Okazaki, K. Fukuda, S. Asakura, T. Shigemori and S. Takahashi, *Sens. Actuators B*, **66**, 142 (2000).
12. J. Villatoro, A. Díez, J.L. Cruz and M.V. Andrés, *Electron. Lett.*, **37**, 1011 (2001).
13. Q. Yan and Y. Liu, *Instrument Technique Sensor*, **4**, 5 (2008).
14. B. Sutapun, M. Tabib-Azar and K. Alex, *Sens. Actuators B*, **60**, 27 (1999).
15. Y. Peng, Y. Tang and J. Sirkis, *SPIE*, **3670**, 42 (1999).
16. X. Bevenot, A. Trouillet, C. Veillas, H. Gagnaire and M. Clément, *Meas. Sci. Technol.*, **13**, 118 (2002).
17. K. Lin, Y. Lu, J. Chen, R. Zheng, P. Wang and H. Ming, *Opt. Express*, **16**, 18599 (2008).
18. C. Perrotton, N. Javahiraly, M. Slaman, B. Dam and P. Meyrueis, *Opt. Express*, **19(S6)**, 1175 (2011).
19. T. Tesfamichael, *IEEE Sens. J.*, **10**, 1796 (2010).
20. S. Nagata, A. Inouye, S. Yamamoto, B. Tsuchiya, K. Takano, K. Toh and T. Shikama, *J. Alloys Comp.*, **446**, 558 (2007).