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Structure and Sensing Properties of Reflective Optical Fiber Hydrogen Sensor

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Keywords : structure, reflective optical fiber sensor, hydrogen, sensing properties.

ABSTRACT

The reflective optical fiber hydrogen sensor has been proposed based on sputtering Tungsten oxide (WO_3) films. This paper focuses on the structure and the sensing properties of the sensor. The theoretic foundations of the sensor were analyzed and the methods of preparing the films were discussed. In order to optimize the performance of the sensor, the gas chamber was design specially and the double optical paths were employed. The testing system of the reflective optical fiber hydrogen sensor was built. The response to hydrogen of the sensor was tested through the experimental system. The results indicate it provided a compact size, economical and effective method to obtain a high sensitivity and excellent repeatability for measuring hydrogen concentration.

INTRODUCTION

Compared with traditional fuels, hydrogen has attracted massive amounts of attention due to the non-pollution characteristics. Currently, it has been widely used in many industrial sectors, such as aerospace, fuel cells, metal smelting and chemical synthesis. Despite the obvious advantages, hydrogen is volatile, flammable and highly combustible, which make the storage, transportation, and manufacturing processes extremely dangerous. When confined in a certain space, it is a direct threat to human life (Salehi A. et al., 2011; Buric M. et al., 2009). Therefore, measuring hydrogen concentration is crucial.

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Many researchers have dedicated themselves in the research and development of the hydrogen sensors. Hübert T. et al. (2011) reviewed the existing major hydrogen sensors, including resistance type, electrochemical type, mechanical type and optical forms. Currently, most commercial hydrogen sensors are based on the electrochemical and mechanical principles, which is commonly applicated in the development of traditional hydrogen sensors. However, these commercial hydrogen sensors are often incapable of meeting the demands of response speed, structure size, stability, restorability and low cost (Palmisano V., 2015; Palmisano V., 2014; Matbouly H.E., 2014).

Due to the excellent performance in potentially explosive atmospheres and the advantages of miniaturization, corrosion resistance and anti-electromagnetic interference (Calavia R. et al., 2010; Weagant S. et al., 2011), optical fiber hydrogen sensor is more promising in leak detection than traditional hydrogen sensors. Several kinds of optical fiber hydrogen sensors, such as micro-mirror sensor, evanescent sensor , surface plasmon resonance sensor, acoustic resonator sensor and fiber Bragg grating sensor, have been proposed in recent years (Dai J.X. et al., 2011; Boudiba A. et al., 2013; Raied K. et al.,2015). Efforts have been made to develop the high performance of optical fiber hydrogen sensors with fast response, high sensitivity, economical costs, and simple structure (Perrotton C. et al.,2013; Oleksenko L.P. et al.,2014, Yu C.B. et al.,2015) However, the performances, such as response time, sensor structure, cross sensitivity and costs(Chan C.C. et al.,2011; Ou J. et al.,2012 ; Westerwaal R. et al., 2013; Hosoki A. et al.,2013; Zhao X. et al.,2015) have hindered the productize of the optical fiber hydrogen sensor.

More to the point, the optical fiber surface or the end surface of these optical fiber hydrogen sensors need to be finely processed. It makes the structure of the sensor very complex and difficult to be manufactured. Compared with other optical fiber hydrogen sensors, the reflective optical fiber hydrogen sensor does not need to carry on the complex processing. It has the advantages in compact structure, easy miniaturization and flexible design. Therefore, a reflective optical fiber hydrogen sensor was proposed in this paper based on the reflection theory. The structure of the reflective optical fiber hydrogen sensor was studied, and the optical properties were discussed.

THE STRUCTURE OF THE REFLECTIVE OPTICAL FIBER HYDROGEN SENSOR

Fundamentals for the Reflective Optical Fiber Hydrogen Sensor

The hydrogen sensitive probe includes the optical fiber and the hydrogen sensitive films, as shown in Figure 1. It can be seen that the incident light generates two processes (transmission and reflection) simultaneously. The reflected light will be directly received by the output optical fiber. Part of the transmitted light which entered the glass substrate will be received by the output optical fiber too. Therefore, the output optical fibers should receive the light intensity reflected directly back from the films and the glass substrate.

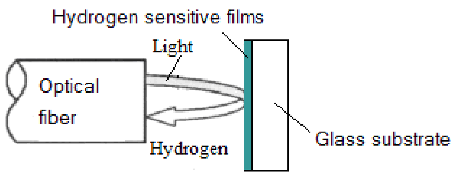

Fig. 1. Optical model of the reflective optical fiber hydrogen sensor.

Preparation of the Films

WO_3 is the most effective hydrogen sensitive material, while palladium (Pd) plays a catalytic role during the hydrogen sensitive films reaction (Fardindoost S. et al., 2010; Boudiba A. et al., 2013). The premiere choice for the reflective optical fiber hydrogen sensors is Pd-doped WO3 films. Sol-gel technique and magnetron sputtering are the most effective methods to prepare hydrogen-sensitive films.

The Sol-gel method is a chemical method for preparing the thin film, and requires the absolute control of various ratio components (Deng, X.L. et al., 2014). Figure 2 shows the image of the optical fiber under a microscope, after being coated by the sol-gel method. From the image, the optical fiber surface appears crack phenomenon.

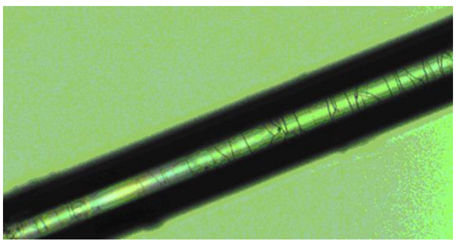

Fig. 2. Hydrogen sensitive films obtained by Sol-gel method.

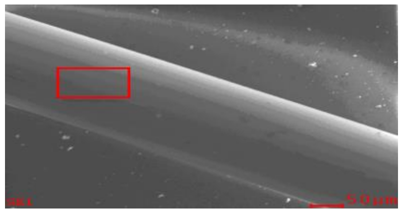

Fig. 3. Hydrogen sensitive films obtained by Magnetron Sputtering.

Magnetron sputtering is a vacuum technique for coating films, which illustrates the enhanced effect and binding force of the films. The magnetron sputtering apparatus is necessary. For the reflective optical fiber hydrogen sensor, materials required include tungsten powder (99.6%), hydrogen peroxide (32%), anhydrous alcohol, acetone and palladium (99.9%). Figure 3 exhibits the films image scanned by an electron microscope.

Optical Path and Gas Chamber

Both the gas chamber and the optical path directly affect the efficiency of the reflective optical fiber hydrogen sensor. Figure 4 shows a diagram outlining the optical structure of the hydrogen sensor.

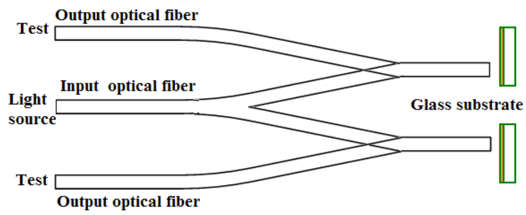

Fig. 4. Optical structure of the reflective optical fiber hydrogen sensor.

The glass substrate sputtered with the hydrogen-sensitive films was be placed in various hydrogen environment. To effectively test the signal changes, a reference path was added to the aid signal change detection. In the presence of external disturbance, both measuring path and the reference path will be affected. The interference issue can be solved by comparing the detection signal difference between the two paths.

The gas chamber is used to implement hydrogen measurement. To the construction of the chamber, the following requirements were carefully considered: isolation of the gas flow for reference part and measurement part, the distance between the

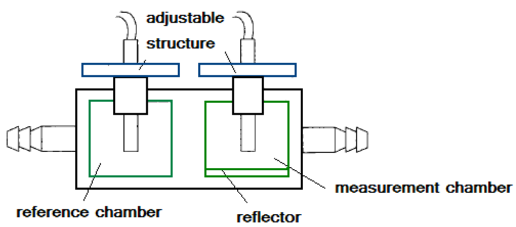

Fig. 5. Structural diagram of gas chamber.

probe and the reflector, and the tilt angle of the reflector. The structure was designed in accordance to the design requirements for a reflective optical fiber hydrogen sensor (Deng, X.L. et al., 2014). Figure 5 depicts a structural diagram, characterizing the gas chamber for the hydrogen sensor. This chamber contains two sections: the reference section and the measurement section. Additionally, the distances between the probe and the reflector are adjustable.

SENSING PROPERTIES OF THE REFLECTIVE OPTICAL FIBER HYDROGEN SENSOR

Optical Testing System

Optical testing system is designed for sensing performance tests on reflective optical fiber hydrogen sensors. The system may be utilized to conduct the following observations: sensor sensitivity, sensor repeatability, other gaseous impurities (such as N_2, natural air) influence on the performance of the reflective optical fiber hydrogen sensor.

Figure 6 exhibits the schematic diagram of the testing system. Essentially, the system is consist of the light source, the reflective probe, the gas chamber, the spectrometer, the gas distribution, and the data processing. The incident light is emitted by a light source and transmitted through the input optical fiber. Eventually, it reaches the gas chamber and is reflected by the gas substrate. Then, the light is received by the outgoing optical fiber. The output information can be obtained by the spectrometer and transmitted to the data processer. The hydrogen concentration into the gas chamber is controlled by the gas distribution, and double optical structures are applied systematically.

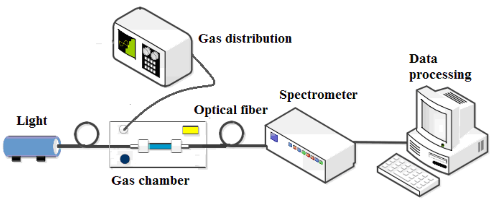

Fig. 6. Schematic diagram of the testing system for the sensor.

Table1 lists the specifics regarding the materials needed to construct the testing system. Magnetron sputtering was selected to coat hydrogen sensitive films, which is used during the hydrogen sensor's manufacturing process. Hydrogen sensitive films, sensor sample and gas chamber were prepared according to the theoretical analysis.

Figure 7 shows the photo of the testing system, which can support the optical characteristics test of the reflective optical fiber hydrogen sensor. The optical fiber coated hydrogen sensitive films is connected light source and the spectrometer respectively. Through the gas distribution device, nitrogen and hydrogen with a certain proportion pass into the chamber. Spectral variation can be displayed on the computer when the hydrogen concentration is changed.

Table1. Equipments and materials for the testing system.

Style name	Brief description
Sensor prototype	Self-control
H_2 sensitive films	Self-control
Reflective probe	R200-7-VIS-NIR
Light source	USB-DT
Spectrometer	USB4000
Gas pressure reducing	outsourcing
H_2 gas standard	99.95%
N_2 gas standard	99.99%
Gas chamber	Self-control
Gas distribution apparatus	CPR001
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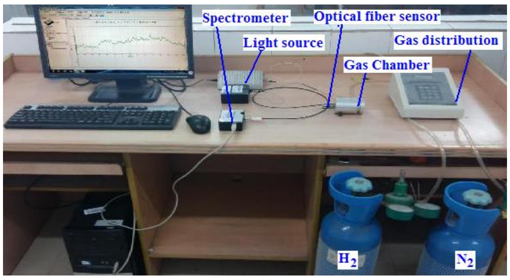

Fig. 7. Experimental test system.

Sensing Properties

The refractive index decreased after applying Pd/WO_3 films absorption hydrogen, and subsequently the optical intensity was reduced. This proves that the optical power of films absorption was minimized, and that the optical intensity of the fiber core was enhanced. Conclusively, the spectral amplitude increased, which is shown in Figure 8. It indicates the light intensity change of the sensor sample was approximately 15%, in the 4% hydrogen atmosphere. The sensor has the capability to effectively detect the presence of hydrogen.

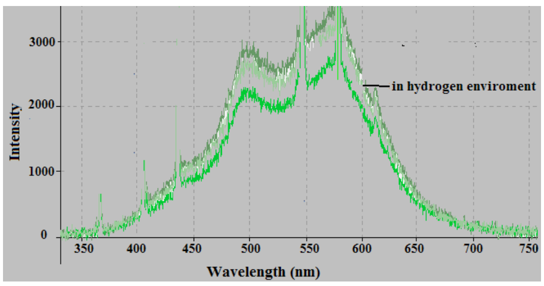

Fig. 8. Spectra after introducing hydrogen

Further experiments show that the reflectivity began to decline with hydrogen injection, and the curve can remain stable after stopping hydrogen injection; the reflectivity began to rise with the release of hydrogen, and the curve can remain stable after the finishing hydrogen release. Figure 9 is the result of introducing and releasing hydrogen twice. Through the experiments of multiple introducing and releasing hydrogen, the reflectance curves obtained by the sensors are consistent at the different wavelength. The results also show the sensor has favorable sensitivity and repeatability.

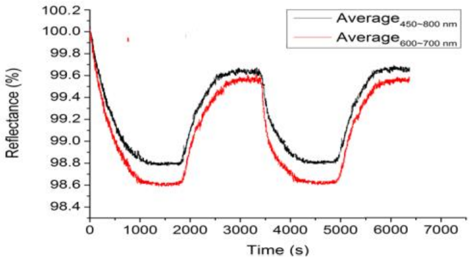

Fig. 9. Response curve after multiple introducing and releasing 4% hydrogen

While in the air environment (nitrogen is about 72% to 78%, and oxygen is about 21% to 27%), and the sensor is not sensitive. There is little change in reflectivity after a long time into the air. The results indicate the sensor has no cross sensitivity.

Figure 10 depicts the hydrogen equilibrium point intensity curve of the two sensor samples in different hydrogen concentration. Due to the change of the distances between the probe and the reflector, the transmittance in absorbing hydrogen of Sample A and Sample B was small differences, but curve's changing trend are basically same. As long as the sensors are well calibrated, they are able to show almost the same sensitivity to hydrogen.

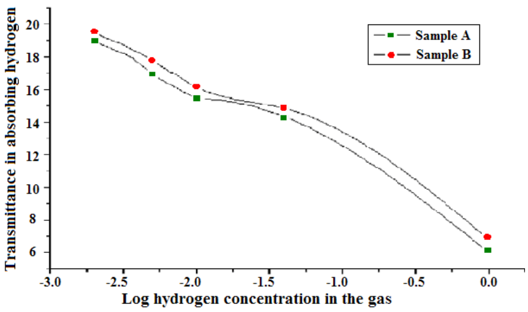

Fig. 10. The hydrogen equilibrium point intensity curve

Through the observation of multiple introducing and releasing 4% hydrogen, the response time was less than 8s and the restoring time was less than 12s, as shown in Figure 11. The fastest response time appears in the third cycle, it was only 3s. Compared with commercial sensors, it has obvious advantages, as shown as Table 2 (Hübert T. et al., 2011). After several cycles, the reflective optical fiber hydrogen sensor responds to hydrogen stably.

At present, electrochemical, semi-conducting and catalytic hydrogen sensors occupy an important

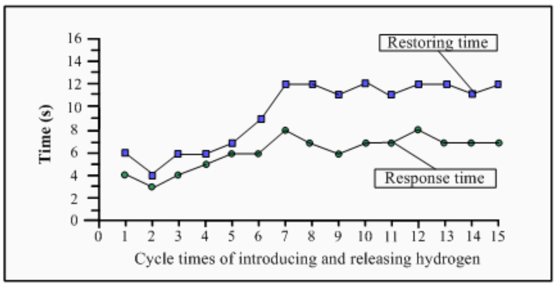

Fig.11. The response time and restoring time of multiple introducing and releasing 4% hydrogen

position in the market. Table 2 lists the comparison of performance specifications with commercially available sensors. In addition to the advantage in response speed, the size of the reflective optical fiber hydrogen sensor was small enough for narrow gap because the optical fiber diameter used for the sensor was only about 200um. Electrochemical, semi-conducting and catalytic hydrogen sensors can not operate in the inflammable and explosive locations because of their work environment (Mu K. et al., 2016). Semi-conducting and catalytic hydrogen sensors are greatly affected by the humidity, temperature or pressure. Compared with these commercial sensors, the reflective optical fiber hydrogen sensor is not only safe, but also anti electromagnetic interference and corrosion resistance. Furthermore, most optical fiber hydrogen sensors are still in laboratory research phase. Compared with other optical fiber hydrogen sensor, the reflective

Table 2. Comparison of performance specifications with commercially available sensors

Sensor type	Response time/s	Size	Work environment	Characteristics
Electro -chemical	<90	Small size	Current or voltage needed	Interference from humidity; Temperature and pressure.
Semi -conducting	<20	Huge volume	Requires O_2 to operate	Poor stability; Interference from humidity and temperature.
Catalytic	<30	Huge volume	Requires O_2 to operate	Sensitive to temperature fluctuations.
The reflective optical fiber sensor	<8	Small enough for narrow gap	Unaffected by electro -magnetic interference	Excellent sensitivity, Stability and restorability; Safety; Simple manufacturing

optical fiber hydrogen sensor is more suitable for mass production, due to the fast response, simple manufacturing process resulting in low cost, and homogeneous sensitive films.

CONCLUSION

In this paper, the structure and sensitivity of the reflective optical fiber hydrogen sensors were investigated. The sensor structure was designed based on the principles of the reflective sensor. Additionally, double optical structure was proposed. The gas chamber included the reference gas chamber and the detection gas chamber. The magnetron sputtering was selected for the hydrogen sensitive films due to its enhanced properties. The measurements indicate that the reflective optical fiber hydrogen sensor maintains acceptable sensitivity and repeatability, and is suited to test hydrogen concentration.

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反射式光纖氫感氣傳感器的結構與傳感特性

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摘 要

本文提出了一種基於濺射氧化鎢（WO3）薄膜的反射式光纖氫氣傳感器。本文主要研究了反射式光纖氫氣傳感器的結構和傳感特性。分析了反射式光纖傳感器的理論基礎，討論了製備氫敏薄膜的方法。為了優化傳感器的效能，設計了特殊氣室，並採用了雙光路。搭建了反射式光纖氫氣傳感器的測試系統，並開展了傳感器的氫敏響應試驗。結果表明，反射式光纖氫氣感測器是一種結構緊湊、經濟有效的測量氫濃度的傳感器，具有高靈敏度和較好的可恢復性。