Optical fiber hydrogen sensor based on light reflection and a palladium-sliver thin film*

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Thin alloy films of palladium (Pd) and silver (Ag) are deposited onto glass substrates via the direct current (DC) magnetron technique. The hydrogen sensor probe consists of optical fiber bundle and Pd/Ag optical thin film. When the sensor is exposed to hydrogen, the refractive index of Pd/Ag optical thin layer will diminish and cause attenuation changes of the reflective light. It is observed that the thickness of Pd/Ag alloy layer can affect the hydrogen sensor signal. Under different substrate temperatures, several Pd/Ag samples are coated with different thicknesses of Pd/Ag alloy, and the results of a hydrogen sensor based on reflective light from the Pd/Ag alloy thin film are discussed.

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A lot of effort has been made to develop high performance hydrogen sensors with fast response, high sensitivity, low cost and simple structure[1-6]. Optical sensors, especially fiber optic sensor technologies provide opportunities for applications of optical hydrogen sensors[3]. Some hydrogen sensor types based on switching the optical properties of Pd or Pd alloy thin films have been reported[4-6].

Meanwhile, the Pd-based hydrogen sensors have poor reliability[7]. Many researchers used the Pd-Ag, Pd-Au, Pd-Ni, Pd-Cr, Pd-Al, and Pd-Cu as the transducer to reduce the embrittlement and provide the longer lifetime for hydrogen sensor. For example, Z. Zhao et al[8] studied the Pd-Au sensor for hydrogen sensing at different temperatures. Y. T. Cheng et al[9] deposited the Pd-Ni alloy on the substrates to detect the hydrogen concentration at ambient temperature. E. Maciak et al[10] used the transition metal oxides to cover palladium film for hydrogen detection. So far, Pd-Ag is perhaps the mostly studied alloy for hydrogen sensing. Min Wang et al[11] fabricated a zigzag-shaped microstructure of Pd-Ag plated on alumina substrate, and the sensing performance of the mixed metal film is much better than that of the pure palladium film. Chandrashekhar G et al[12] investigated the diffusivity and permeability of hydrogen in palladium-silver and palladium-gold (Au) over a wide temperature range, and found that the Pd-Ag alloy system exhibits good time response and better mechanical strength, and it overcomes the problem of hydrogen embrittlement for pure palladium metal. So the Pd-Ag alloy plays an important role on the sensing material for hydrogen detection. Compared with other Pd alloys, Pd-Ag thin film can provide better sensing properties for hydrogen.

In this paper, we report an optical fiber hydrogen sensor based on Pd-Ag alloy and light reflection. Compared with traditional structure of hydrogen sensor, the proposed configuration based on the light reflection of Pd-Ag thin film can provide higher signal-to-noise for optical fiber hydrogen sensor.

The performance of the optical fiber hydrogen sensor is tested with the experiment setup (see Fig.1) which consists of testing gas chamber, sensor probe, signal processing, and hydrogen mixing & adjusting apparatus. A LED transmitter (Agilent HFBR-1527) driven by a carrier wave generator illuminates the transmitting fiber bundle. The optical signals reflected back into two receiving fiber bundles are detected by two identical PIN receivers (Agilent HFBR-2526), each of which contains a PIN photodiode and trans-impedance preamplifier circuit with a responsivity of 5 mV/μW. The Pd-Ag thin films are evaporated on the optical glass sub-

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strates in vacuum as the hydrogen sensing media. The hydrogen mixing and adjusting apparatus helps to achieve the base-line and realize the constant gas input. The gas chamber is composed of two separated gas cells in Fig.1. One of the gas cells is considered as the reference cell in the experiment, and the hydrogen is injected into the test chamber. The sensor probe is the important part in the system. According to certain discipline, the sensor probe consists of lots of optical fibers to form the coaxial optical fiber bundle. The fibers in the center of the sensor are transmitting fibers, and the others are receiving fibers.

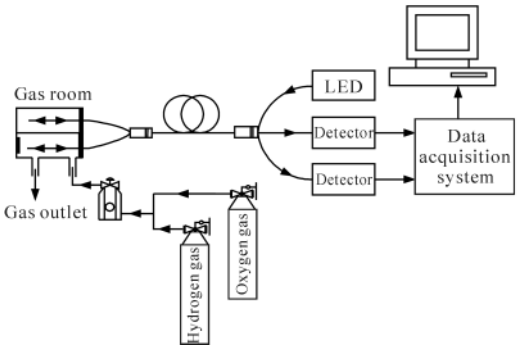

Fig.1 Experimental setup for testing the performance of the optical fiber bundle hydrogen sensor

The preparation of Pd-Ag alloy membranes is carried out in a commercial magnetron sputtering machine (FJL560) equipped with DC and RF power sources and an adjustable substrate stage in Wuhan University.

Fig.2 is a representation of the magnetron sputtering deposition unit. Before actual deposition, the pre-sputtering is done for several minutes by masking the substrate to stabilize the plasma power at the desired value by means of a shutter. It's important for the morphological uniformity of Pd-Ag alloy thin films.

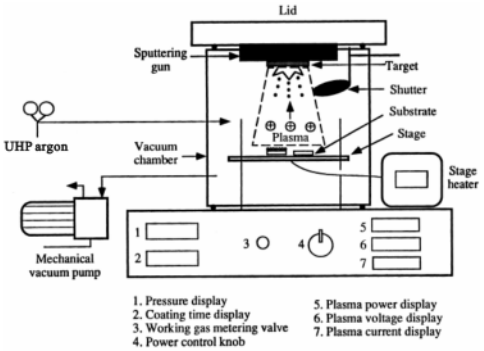

Fig.2 Representation of the magnetron sputtering deposition system

The hydrogen sensing probe consists of optical fiber bundle and Pd-Ag alloy thin film. Fig.3 is the optical model of the reflective optical fiber bundle hydrogen sensor.

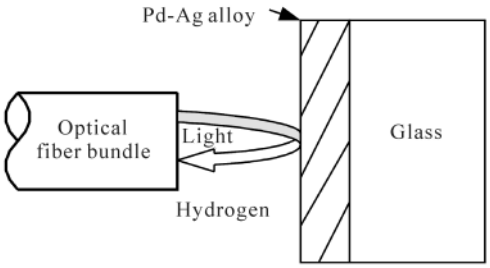

Fig.3 Optical model of the reflective optical fiber bundle hydrogen sensor

In the optical model of hydrogen sensor, n_{air}=1, is the refractive index of air, n_{alloy}=1.79 + 4.38i[13], is the complex refractive index of Pd-Ag alloy, and n_{glass}=1.775 is the refractive index of glass substrate. Reflected light is received by optical fiber bundle directly, and due to the transmitting process of light in Pd-Ag alloy thin film, a part of transmitted light will enter the Pd-Ag thin film to modify the optical constant of the alloy. In the boundary of gas–Pd-Ag alloy–glass, the reflectivity R_1 of Pd-Ag alloy is described by

$$R_1 = \left| \frac{r_1 + r_2 \exp(-\mathrm{i}\varphi)}{1 + r_1 r_2 \exp(-\mathrm{i}\varphi)} \right|^2 . \tag{1}$$

According to the conception of Fresnel reflectance, r_1 and r_2 are described by the following equations respectively

$$r_1 = \frac{n_{air} - n_{alloy}}{n_{air} + n_{alloy}} , \tag{2}$$

$$r_2 = \frac{n_{alloy} - n_{glass}}{n_{alloy} + n_{glass}} . \tag{3}$$

φ is the phase shift of Pd-Ag thin film in Eq.(1), d is the thickness of Pd-Ag alloy on the glass, and λ is the wavelength of incident light, so we have

$$\varphi = \frac{4\pi n_{alloy} d}{\lambda} . \tag{4}$$

Meanwhile, the transmitted light in the boundary of glass–Pd-Ag alloy–gas will under the reflected phenomena continuously, and the reflectivity R_2 of Pd-Ag alloy is described by

$$R_2 = \left| \frac{r_1' + r_2' \exp(-\mathrm{i}\varphi)}{1 + r_1' r_2' \exp(-\mathrm{i}\varphi)} \right|^2 , \tag{5}$$

where

$$r_1' = \frac{n_{\text{glass}} - n_{\text{alloy}}}{n_{\text{glass}} + n_{\text{alloy}}} \quad , \tag{6}$$

$$r_2' = \frac{n_{\text{alloy}} - n_{\text{air}}}{n_{\text{alloy}} + n_{\text{air}}} \quad . \tag{7}$$

On the two reflective boundaries, R_1 and R_2 follow the rules of $0<|R_1|<1$ and $0<|R_2|<1$, respectively. So the whole reflectivity R of Pd-Ag alloy thin film in sensor probe could be summarized by

$$R = R_1 + \frac{R_2(1-R_1)^2}{1-R_1R_2} \quad . \tag{8}$$

Through Eq.(8), the optimal thickness of Pd-Ag alloy is simulated in Matlab.

From Fig.4, we can conclude that the optimal Pd-Ag alloy sputtering thickness is 20−30 nm for the optical fiber bundle hydrogen sensor when the light wavelength is λ=650 nm. When the thickness of alloy is under 8 nm, the mechanical intensity of thin film is so weak and the Pd-Ag is more easily saturated in the hydrogen atmosphere. It's not the practical value for hydrogen sensor. At the same time, when the thickness of Pd-Ag alloy exceeds 30 nm, the reflectivity R decreases significantly. The main reason is that the absorption time and desorption time will increase, and the sensitivity of the hydrogen sensor decreases largely.

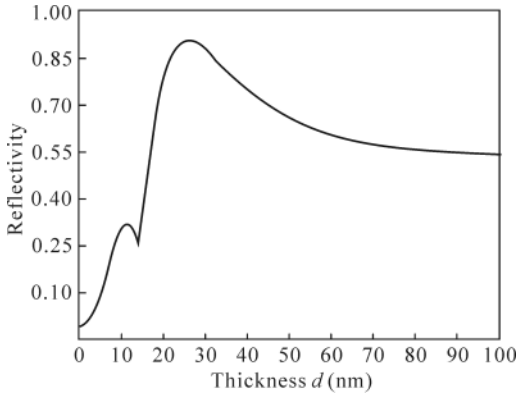

Fig.4 Simulation curve between reflectivity *R* and sputtering thickness *d* of Pd-Ag alloy thin film

According to the relevant sputtering parameters mentioned in Ref.[14], under a constant sputtering deposition rate, the metal film thickness is proportional to the deposition time, and the target-substrate distance may also be an important factor but it is fixed at 6.8 cm in this study. The thickness of Pd-Ag alloy is measured by Kla–Tencor P16+ nanometer surface profiler. At the normal temperature (300 K), the Pd-Ag alloy film is sputtered for 5 min, 10 min, and 15 min in succession and under 10 W DC plasma power from Pd-Ag alloy target.

In Tab.1, testing results indicate that the sputtering thickness of Pd-Ag is linear with sputtering time. Typically 10 min is required to achieve the 20−30 nm Pd-Ag alloy film on the substrate. At the same time, the variance of Pd-Ag thickness is very little under the fixed sputtering time. Fig.5 is the testing result of Pd-Ag thin film sample prepared by sputtering for 10 min.

Tab.1 Effect of sputtering time on the Pd-Ag alloy membranes made by DC sputtering

Sputtering time		5 min	10 min	15 min
Sputtering thickness	Sample 1	15.4 nm	21.22 nm	51.62 nm
	Sample 2	17.48 nm	24.64 nm	50.68 nm
	Sample 3	16.24 nm	22.23 nm	50.79 nm

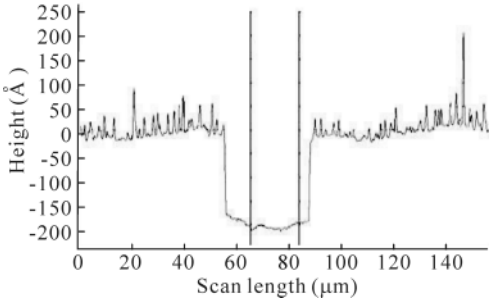

Fig.5 Testing result of Pd-Ag membranes on surface profiler, prepared by sputtering for 10 min, under substrate temperature of 300 K and 10 W plasma power

At ambient temperature and pressure, the Pd-Ag alloy thin films with different thicknesses are used as sensing media to detect the hydrogen. The sensing properties of hydrogen sensor are recorded by LabVIEW real-timely in the 4.1% hydrogen atmosphere. In Fig.6(b) we notice that the hydrogen sensor signal changes as the hydrogen concentration changes, and 22.15 nm Pd-Ag alloy thin film exhibits good magnitude response and short response time. From Fig.6(a) we can also notice that the sensitivity depends on the thickness of the film deposited on the substrate. The thinner the Pd-Ag alloy film as sensing material, the shorter the response time and the better the sensitivity. Nevertheless, compared with Fig.6(b), the amplitude response of Pd-Ag in Fig.6(a) is very small. In Fig.6(c), it's concluded that the thicker the Pd-Ag alloy film, the better the amplitude response, but the response time is very long. So the thickness of Pd-Ag alloy layer is increased, and the sensor response to hydrogen concentration changes becomes less noticeable. The main reason is that the formative PdH_x is hard to change the thicker Pd-Ag film, and finally retards the reflectivity changes in Pd-Ag thin film. Comprehensively considering amplitude response and response time of reflective optical fiber hydro-

gen sensor, 20-30 nm Pd-Ag alloy thin film is the best sensing medium for optical fiber hydrogen sensor. And a series of experiments also prove that 20-30 nm Pd-Ag is suitable for the sensing media of hydrogen sensor. The experimental results are consistent with the theoretical simulations in Fig.6.

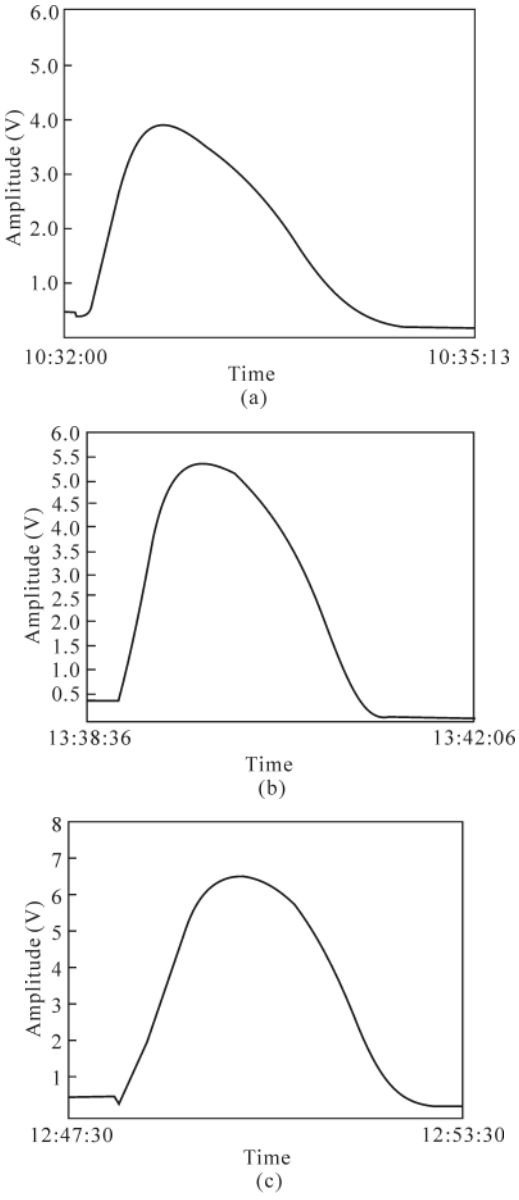

Fig.6 Under normal conditions, experimental amplitude response and response time for three Pd-Ag film samples with different thicknesses: (a) 15.4 nm; (b) 22.15 nm; (c) 50.79 nm

In the paper, we have demonstrated a novel reflective optical fiber hydrogen sensor based on Pd-Ag alloy. The Pd-Ag alloy could eliminate the hydrogen embrittlement in sensor. Samples with different thicknesses are deposited by DC sputtering. Through the relevant testing experiment, we summarize some key parameters in sputtering process, which are expected to affect the morphology of Pd-Ag alloy membranes prepared by DC magnetron sputtering. At the same time, through the theoretical simulations and experiments, we analyze the thickness effect on hydrogen sensor. They are in good agreement between theoretical simulation and experimental results. So the sensor has the potential to detect hydrogen concentration and leakage points.

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