Experimental study on optical fiber bundle hydrogen sensor based on palladium-silver optical thin film*

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In this paper, a 20 nm palladium-silver (Pd/Ag) ultrathin optical film is used for hydrogen gas sensing. The mole ratio of the two metals is controlled at Pd:Ag=3:1. In the direct current (DC) sputtering machine, the optical thin film is evaporated on the optical glass. Compared with pure palladium, the Pd/Ag alloy can increase the life and the stability of the sensing film. Optimum sputtering parameters for Pd/Ag alloy are presented in this paper, and the effects of different experimental conditions for hydrogen sensor are investigated, including the temperature effect, humidity effect and cross sensitivity of hydrogen sensor for different gases. The experiment results indicate that the hydrogen sensor based on Pd/Ag optical thin film exhibits good sensing characteristics. The existing of CO and water in hydrogen increases the response time and decreases the response amplitude of optical fiber bundle hydrogen sensor. The experiment results show that the increasing temperature can eliminate the effect and shorten hydrogen sensor response time effectively.

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The development of aeronautics, sustainable energy systems and sustainable transport technologies drives the use of hydrogen as energy carrier[1]. In the last years, lots of efforts have been made to develop high-performance hydrogen sensors with safety and longer life, most of which are based on electrical techniques for detection[2]. Optical techniques seem to be more attractive in hazardous atmospheres owing to the lack of sparking possibilities. Fiber optic sensors provide opportunities for applications of optical sensors[3]. Most of the optical fiber sensors use palladium (Pd) film as transducer to detect the concentration of hydrogen. However, although pure palladium sensors could provide the good hydrogen sensitivity, there are some drawbacks associated with pure palladium. During the process of absorption and adsorption in hydrogen, pure palladium film suffers the embrittlement phenomenon, the metal morphology of pure palladium undergoes the $\alpha \rightarrow \beta$ phase transformation, and the process is irreversible. After several cycles of exposure to hydrogen, the palladium breaks off from the substrate. So in order to overcome the problem, a great number of experiment reports introduced other metals to form palladium alloy. Several authors[4-6] introduced the second group metals (Ni, Ag, Cu) into the palladium to form alloy optical film. The Pd/Ag and Pd/Ni alloys could overcome the problem of hydrogen embrittlement. So far, Pd/Ag is perhaps the mostly studied alloy for hydrogen sensing. Wang[7] 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 pure palladium film. So 20 nm $Pd_{75}Ag_{25}$ ultrathin films evaporated on the float glass substrates are adopted to overcome the hydrogen embrittlement. In this paper, we report the preparation and characterization of a hydrogen sensor, and the response time and steady-state response values are measured as a function of hydrogen concentration at different atmospheres. The effects of temperature and cross sensitivity (CO, oxygen and nitrogen) for the sensor are also discussed.

The preparation of Pd/Ag alloy membranes was carried out in a commercial magnetron sputtering machine (FJL560) equipped with DC and radio frequency (RF) power sources, adjustable substrate stage and heating capability up to 400 °C.

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Fig.1 is the schematic diagram of the magnetron sputtering deposition unit. Before actual deposition, pre-sputtering was done for several minutes by means of a shutter. The step was necessary to stabilize the plasma power at the desired value before actual deposition started. Tab.1 gives the optimized experiment parameters for DC magnetron sputtering. In order to enhance the adhesive attraction between the Pd/Ag and substrate, there is about the 5 nm sputtered Ti on the surface of the glass substrate. In Tab.1, the sputtering time depends on the DC sputtering power, and under the fixed sputtering power, the thickness of film depends on the sputtering time.

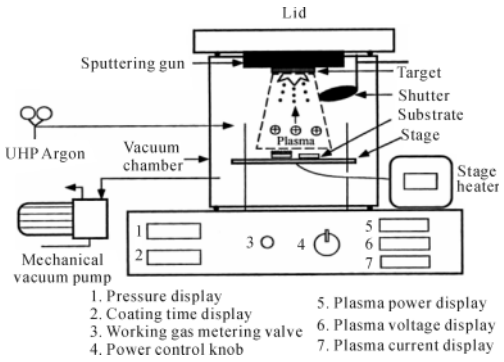


Fig.1 Schematic diagram of magnetron sputtering deposition system

Tab.1 Sputtering parameters for Pd/Ag alloy

Target	75%Pd-25%Ag alloy
DC power (W)	10−60
Sputtering distance (mm)	6.8
Substrate temperature (K)	673
Base pressure (Pa)	1.2×10^{-3}
Ar gas flow rate (sccm)	5−10
Working pressure (Pa)	0.5−1.2
Sputtering time (min)	1−10
Target thickness (nm)	20

Fig.2 illustrates the schematic diagram of the sensor testing station. The performance of optical fiber hydrogen sensor is tested with the experiment setup which is made up of several parts: testing gas chamber, sensor probe, signal processing, and hydrogen mixing & adjusting apparatus. An 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 a trans-impedance preamplifier circuit with the responsivity of 5 mV/μW. According to the parameters in Tab.1, the 20 nm $Pd_{75}Ag_{25}$ thin films were evaporated on the optical glass substrates in vacuum as the hydrogen sensing films. The hydrogen mixing and adjusting apparatus helps to achieve the base-line and realize the constant gas input, and the gas chamber is composed of two separated gas cells as shown Fig.2. One of the gas cells is considered as the reference cell in the experiment, and the hydrogen is injected into 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.

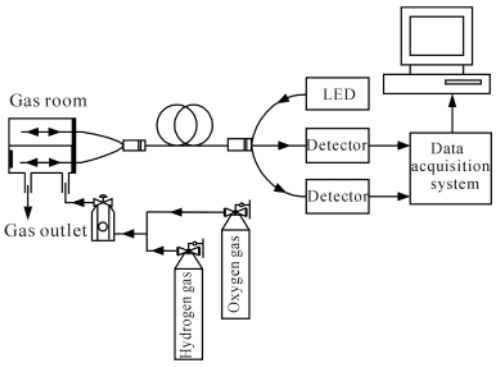


Fig.2 Experimental setup for optical fiber bundle hydrogen sensor

In the paper of Buelter[8], the useful reflective light was very weak, and most of light from the source was transmitted through the palladium film and lost at last. Compared with the model brought forward by Buelter, the novel reflective optical fiber bundle hydrogen sensor can provide high density reflective light which contains the information of hydrogen concentration, and it's convenient for the subsequent signal-processing.

The transmitting and receiving fibers in sensor probe have the same numerical aperture (*NA*). So the output voltages of V_1 and V_2 of two receiving optical signals processed by the experimental circuits are written by

$$V_1 = K_1 G_1 R \delta_1 P_0 f(d_1),\ V_2 = K_2 G_2 R \delta_2 P_0 f(d_2)\ , \qquad (1)$$

where K_i is the ratio of light splitting, and $K_1 = K_2 = 50\%$. G_i is the voltage gain, R is the vibration influence coefficient, δ_i is the reflective ratio of Pd-Ag film and reference surface, P_0 is the light density from the LED, and d_i is the reflective distance from the sensor probe to reflective surface. The receiving fibers could receive the maximum light density for the coaxial optical sensor probe when $d_1 = d_2 = 1$ mm, and $f(\bullet)$ is the modulation characteristic function of the optical fiber bundle[9]. The ratio of the two receiving signals is obtained as

$$\Gamma = V_1/V_2 = [K_1 G_1 R \delta_1 P_0 f(d_1)] / [K_2 G_2 R \delta_2 P_0 f(d_2)] = \{[G_1 f(d_1)]/[G_2 \delta_2 f(d_2)]\} \times \delta_1\ , \qquad (2)$$

where dimensionless parameter Γ represents the concentration of hydrogen, δ_1 changes along with the hydrogen concentration when palladium exposed to the hydrogen, and G_1, G_2, $f(d_1)$, $f(d_2)$ and δ_2 are constants in the equation.

The performance of $Pd_{75}Ag_{25}$ thin film hydrogen sensor is tested using the experiment setup depicted in Fig.1. Both air and hydrogen flow rates are controlled by using the flow meters. Two sensor probes are inserted into the two separated cells. The experiments are carried out at ambient temperature and pressure. Basically, the sensors are exposed to several different concentrations of hydrogen ranging from 1% to 3.99%, and the signal response as a function of hydrogen concentration is shown in Fig.3. The hydrogen sensor is provided with good linearity.

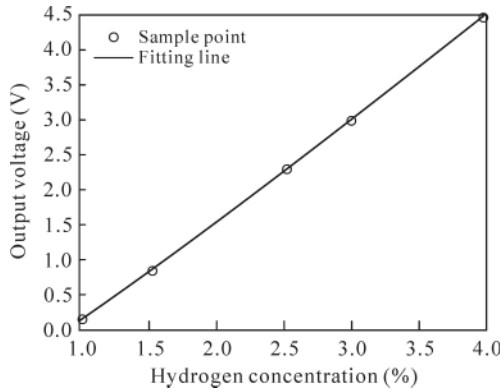
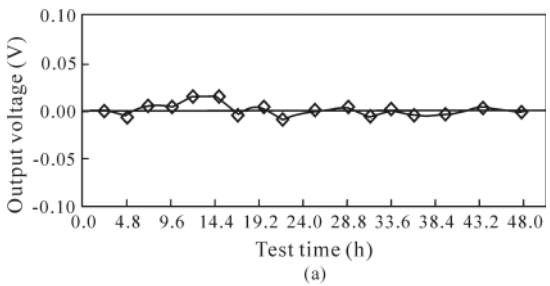


Fig.3 Signal response vs. hydrogen concentration

Reliability testing is very important for the optical fiber hydrogen sensor, so a series of experiments are carried out to survey the reliability. The palladium-sliver alloy is tested in air and in 2.54% hydrogen at ambient temperature over 48 h. As we can see in Fig.4, the hydrogen sensor output tends to flat along with the reaction time. The signal response has an acceptable level of variance, and the signal response standard deviation varies by 0.36% and 2.43% at room temperature. The hydrogen sensor has high stability. In further hydrogen switch-on and -off tests, the optical hydrogen sensor responses are also recorded for 3.99% hydrogen at room temperature. The output peak values are almost the same and demonstrate high reliability for hydrogen sensor as shown in Fig.5.



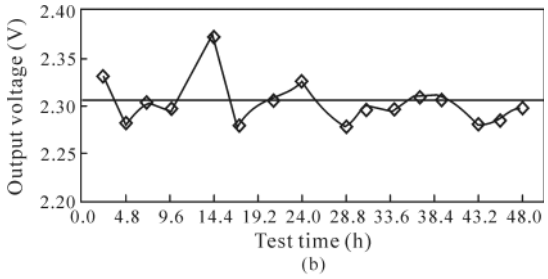


Fig.4 Reliability measurements in (a) air and (b) 2.54% hydrogen at ambient temperature and pressure

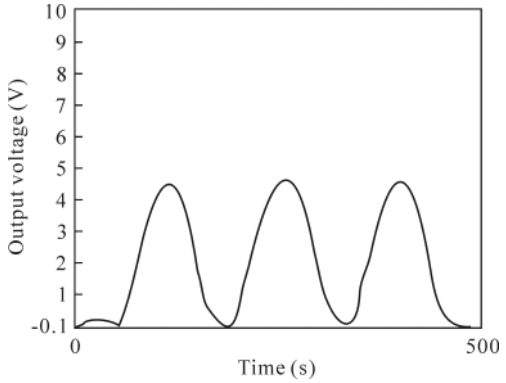


Fig.5 Reliability measurement in 3.99% hydrogen at ambient temperature and pressure

The relative humidity is an influence factor for optical fiber sensor, so lots of experiments are tested at normal temperature and pressure, and the signal response of hydrogen sensor is recorded by Labview in computer. In order to test reversibility capability of hydrogen sensor, when the hydrogen sensor's amplitude reaches the maximum value, the mixture gas of H_2O and H_2 is shut down immediately. Fig.6 shows that the hydrogen sensor can go back to its primary state, and exhibits good recovery capability.

As we can see in Fig.6, compared with sensor's sensing characteristics in dry condition, the sensor response amplitude in humidity atmosphere is decreased by 10%. Due to the water in hydrogen, relative humidity affects the performance of optical hydrogen sensor. The existing water is adsorbed on the optical thin film surface to form OH molecules with assistance of surface atomic oxygen. The reaction between the hydrogen molecule and OH dominates the consumption of hydrogen gas for forming the water on surface of thin film, thereby reducing the formation of PdH_x. As long as water molecules do occur on the surface of Pd-Ag thin film, the process of absorption/desorption may retard largely. At the same time, water molecules accelerate the ageing of Pd/Ag alloy optical film. However, the elevated temperature can reduce the influence of relative humidity on the hydrogen sensor. Therefore, in further investigations, more attention should be focused on the protection of Pd/Ag film in an

atmosphere with high humidity.

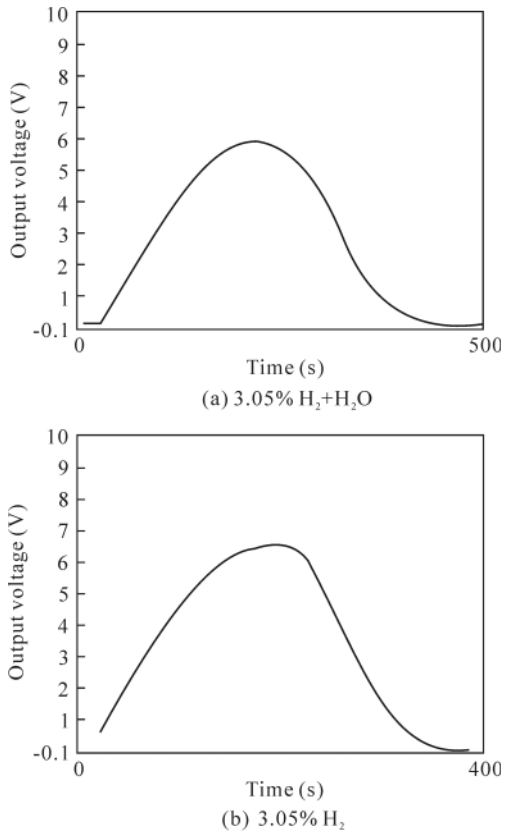


Fig.6 Humidity influence measurements in 3.05% hydrogen with and without water at ambient temperature and pressure

It's important for hydrogen sensor to test the cross sensitivity for other gases at normal temperature. The test results are recorded by Labview. Similarly, it is indicated that the sensor exhibits good recovery capability when it is isolated from the hydrogen atmosphere.

In Fig.7, the optical fiber bundle hydrogen sensor exhibits the same response performance in CO_2+H_2, N_2+H_2 and O_2+H_2 circumstance, and CO_2, N_2 and O_2 have no influence on optical thin film. However, due to the CO poisoning phenomenon, the experiment with CO retards the response time largely at ambient temperature, and the phenomenon is similar to the humidity effect. CO can bind the palladium film, thus increase the response time and reduce response amplitude largely. The experiments for hydrogen and CO are tested in high temperature environment, so we can conclude that the CO poisoning phenomenon in the test could be overcome by increasing the testing temperature, and the effect of CO poisoning phenomenon can become negligible in experiment. The increasing temperature could speed up the hydrogen absorption and CO desorption on the Pd/Ag alloy surface.

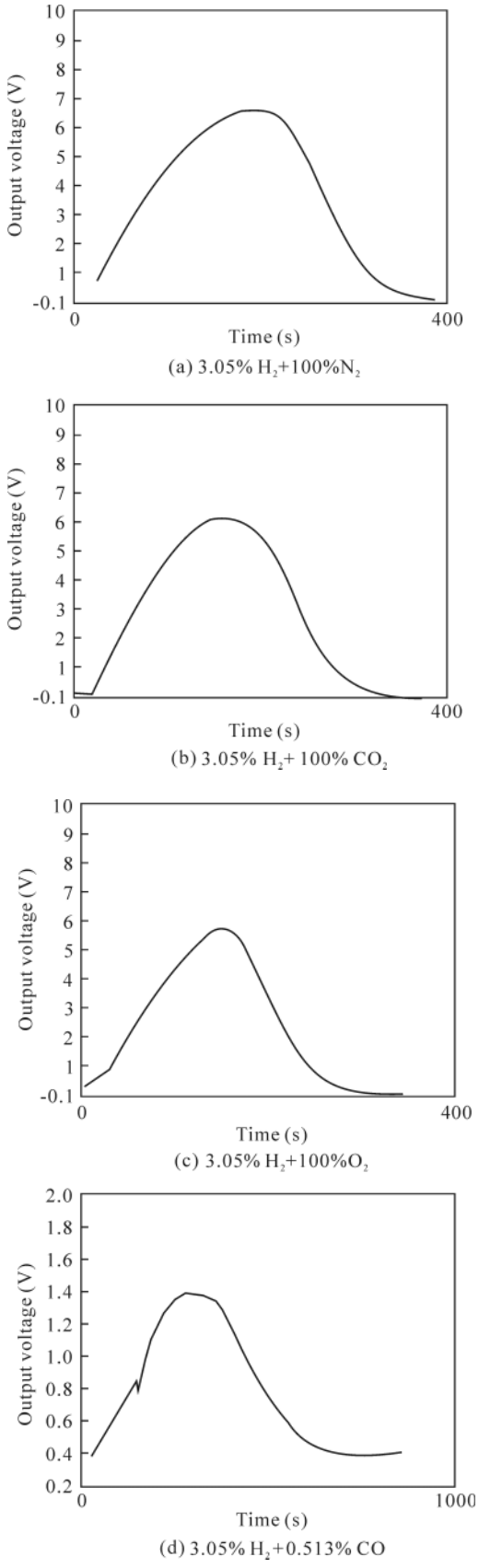


Fig.7 Cross sensitivity measurements for 3.05% hydrogen and other different gases at ambient temperature and pressure

It can be found that working temperature of sensor has a significant effect on sensor performance. Fig.8 shows the signal response at different temperatures ranging from 10 °C to 80 °C for 3.99% hydrogen. All the observations suggest that increasing the temperature can accelerate the movement velocity of hydrogen atoms and speed up the desorption of hydrogen atoms on the palladium-silver film. As shown in Fig. 8, the response time and response amplitude decrease with rising temperature, and the main reason is the decrease in solubility of hydrogen and the formation of the hydride in the optical thin film based on palladium-silver alloy.

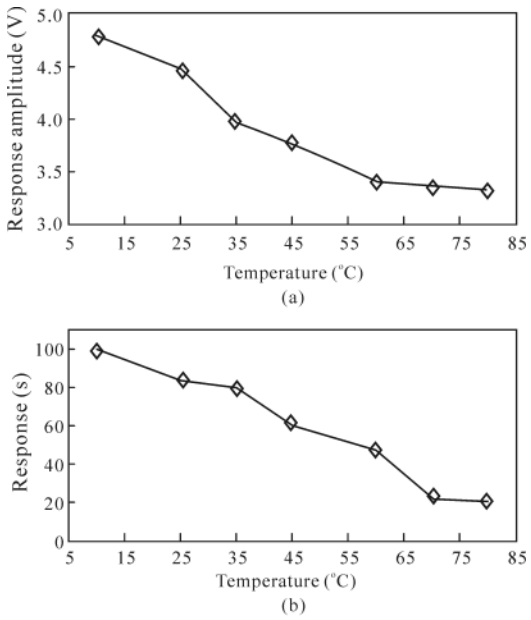


Fig.8 (a) Response amplitude and (b) response time vs. temperature for 3.99% hydrogen in a balance of air at normal pressure

In summary, we characterize the hydrogen sensing properties of 20 nm-thick $Pd_{75}Ag_{25}$ thin films through utilizing DC plasma sputtering technique. The response amplitude increases proportionally with the hydrogen concentration, and the hydrogen sensor shows good stability and lifetime at room temperature and pressure. At the same time, there are several further experiments to be done to find potential approaches to eliminate the CO poisoning phenomenon and humidity effects for hydrogen sensor based on Pd/Ag alloy.

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