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.

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 adorption in hydrogen, pure palladium film suffers the embrittlement phenomenon, the metal morphology of pure palladium undergoes the α → β 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 ºC.

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Fig. 1 is the schematic diagram of the magnetron sputtering deposition unit. Before actual deposition, presputtering 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. 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/PW. According to the parameters in Tab. 1, the 20 nm Pd75Ag25 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. 1 Schematic diagram of magnetron sputtering deposition system](image1)

Fig. 1 Schematic diagram of magnetron sputtering deposition system

<table>
<thead>
<tr>
<th>Target</th>
<th>75%Pd-25%Ag alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC power (W)</td>
<td>10–60</td>
</tr>
<tr>
<td>Sputtering distance (mm)</td>
<td>6.8</td>
</tr>
<tr>
<td>Substrate temperature (K)</td>
<td>673</td>
</tr>
<tr>
<td>Base pressure (Pa)</td>
<td>1.2 × 10⁻¹</td>
</tr>
<tr>
<td>Ar gas flow rate (sccm)</td>
<td>5–10</td>
</tr>
<tr>
<td>Working pressure (Pa)</td>
<td>0.5–1.2</td>
</tr>
<tr>
<td>Sputtering time (min)</td>
<td>1–10</td>
</tr>
<tr>
<td>Target thickness (nm)</td>
<td>20</td>
</tr>
</tbody>
</table>

Tab. 1 Sputtering parameters for Pd/Ag alloy

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

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

where $K_1$ is the ratio of light splitting, and $K_2 = K_2 = 50\%$. $G_1$ is the voltage gain, $R$ is the vibration influence coefficient, $\delta_1$ 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 $f(\cdot)$ is the modulation characteristic function of the optical fiber bundle[9]. The ratio of the two receiving signals is obtained as

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

where

$$f(d) = (d/d_0)^{1/2}$$

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