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Experimental research of optical fiber hydrogen gas sensing system based on palladium-silver alloy*

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A novel optical fiber hydrogen sensing system based on palladium (Pd) and sliver (Ag) is proposed. By direct current (DC) magnetron process, Pd/Ag alloy ultra-thin films were deposited on the substrate to eliminate the hydrogen embrittlement of sensor based on pure Pd. Several samples with different thin film thicknesses were fabricated at different substrate temperatures and tested in the optical fiber hydrogen sensor setup. We do a series of experiments for obtaining optimum sputtering parameters, such as optimum sputtering temperature and thickness of Pd/Ag alloy film. The humidity effect and reliability experiment for the optical fiber hydrogen gas sensor are reported in detail. The testing results demonstrate the Pd/Ag alloy is a promising material for optical fiber hydrogen gas sensor.

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Hydrogen (H_2) is a renewable energy source and has many applications, such as chemical production and fuel cell technology. It has experienced an increased interest around the world due to its potential as green energy[1]. In the last years, lots of efforts have been made to develop high performance hydrogen gas sensors with safety and longer life. However, most of them are based on electrical detection techniques[2]. Optical techniques seem to be more attractive in hazardous atmosphere owing to the lack of sparking possibility. Optical sensors and especially fiber optic sensor technology provide opportunities for applications of optical hydrogen sensors[3]. Due to its high sensitivity and selectivity towards hydrogen, pure palladium (Pd) is the most promising candidate, and is commonly used as sensing material for hydrogen gas sensor. Meanwhile, there are some drawbacks associated with pure palladium. Besides its long response time, Pd-based hydrogen sensors have poor reliability, due to the material instability resulting from the large volume changes that occur during phase transition[4,5]. During the process of absorption and adsorption in hydrogen, pure Pd film suffers the hydrogen embrittlement phenomenon. Then the morphology of pure Pd undergoes the phase transformations which are irreversible, and the Pd transformations affect the lifetime and reliability of hydrogen gas sensor. Some researchers[6-8] presented several Pd-alloys as the sensing materials for hydrogen gas sensors. Pd/Ag, Pd/WO_3 and Pd/Ni alloys could overcome the hydrogen embrittlement problem. So far, Pd/Ag is perhaps the mostly studied alloy for hydrogen sensing. So here we adopt Pd/Ag ultra-thin films evaporated on the glass substrates in the optical fiber bundle hydrogen gas sensor to overcome the well-known problem of hydrogen embrittlement.

In this paper, a novel optical fiber hydrogen gas sensing system based on Pd/Ag alloy is proposed. The paper focuses on the optimization of membrane thickness, sputtering temperature, membrane reliability and humidity effect for optical fiber hydrogen sensor, and its sensing characteristics and optimum sputtering parameters are investigated and discussed.

The Pd/Ag alloy membranes were prepared by a commercial magnetron sputtering machine (FJL560) equipped with direct current (DC) power sources and an adjustable substrate stage in Wuhan University. The Pd/Ag alloy membranes were sputtered on the glass, and the glass was inserted vertically with the substrate as shown in Fig.1.

Fig.1 illustrates the fabrication of optical path for reflective optical fiber hydrogen gas sensor. The reflectivity of the Pd/Ag alloy membranes changes with the hydrogen concentration around the Pd/Ag alloy. The implementation system of optical fiber path has several advantages as follows. Firstly, the concentration of hydrogen depends on the reflectivity of Pd/Ag alloy membrane. Secondly, the disturbance caused by the fluctuation of LED light source and the loss of optical fiber transmitting is eliminated by taking a ratio of two PIN receiving signals.

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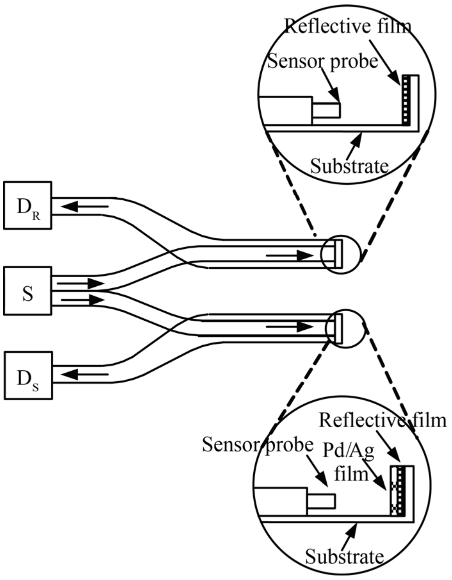


Fig.1 Schematic diagram of optical path for optical fiber hydrogen gas sensor

So through detecting the changes of reflective light intensity in the Pd/Ag alloy membrane, the hydrogen gas concentration can be calculated indirectly. It is concluded that the reflectivity of Pd/Ag alloy membrane plays an important role for the optical fiber hydrogen gas sensor.

Fig.2 illustrates the schematic diagram of the sensor testing station. The performance of optical fiber hydrogen gas sensor was tested with the experimental setup which is made up of testing gas chamber, sensor probe, signal processing and hydrogen mixing and adjusting devices. A light-emitting diode (LED) source (S) driven by a carrier wave generator illuminates the transmitting optical fiber bundle. The optical signals, which are reflected back into two receiving fiber bundles, are detected by two identical O/E detectors (D_S and D_R), each of which contains a PIN photodiode and trans-impedance preamplifier circuit with the responsivity of 5 mV/μW. According to the sputtering parameters, the Pd/Ag thin films with thickness of 20—30 nm are evaporated on the glass substrates in vacuum as the hydrogen sensing medium. The hydrogen mixing and adjusting devices help to achieve the base-line and realize the constant gas input of hydrogen gas sensor. The gas chamber is composed of two separated gas cells as shown in Fig.2. 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 optical fibers, and the others are receiving optical fibers.

According to the sputtering parameters in Tab.2, with a constant sputtering deposition rate, the metal film thickness is proportional to the deposition time. The target-substrate distance of 6.8 cm is constant here. The thickness of Pd/Ag alloy was measured by Kla-Tencor P16+ nanometer Surface Profiler. At the normal temperature (300 K), Pd/Ag alloy films were obtained by sputtering for 5 min, 10 min and 15 min in succession and under 10 W DC plasma power from Pd/Ag alloy target.

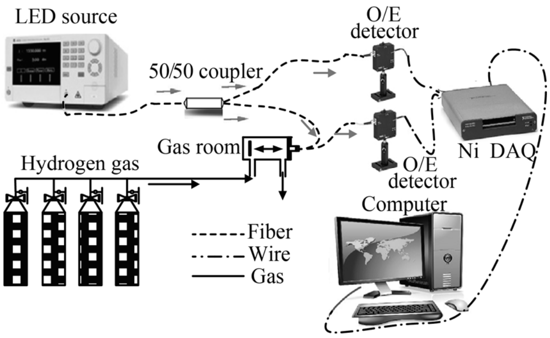


Fig.2 Experimental setup for optical fiber hydrogen gas sensor

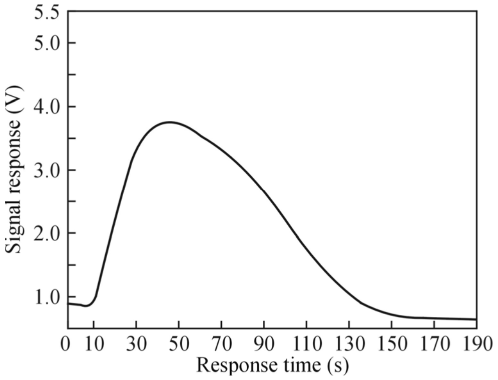
Tab.2 Thicknesses of Pd/Ag alloy thin films with different sputtering time in three times

Sputtering time	5 min	10 min	15 min
I	15.40 nm	21.22 nm	51.62 nm
II	17.48 nm	24.64 nm	50.68 nm
III	16.24 nm	22.23 nm	50.79 nm

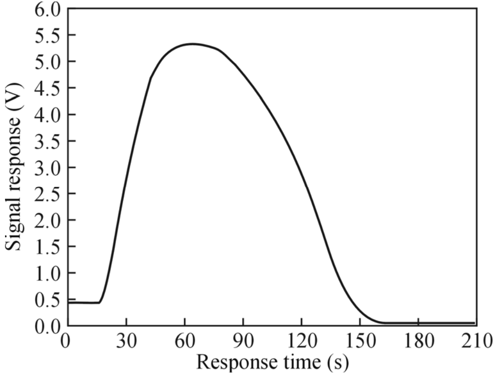
According to the theoretical calculation in the previous paper[9,10], it's concluded that Pd/Ag alloy film with thickness of 20—30 nm is suitable as the sensing medium of hydrogen gas sensor. In Tab.2, testing results indicate that 10 min is required to achieve the Pd/Ag alloy film with thickness of 20—30 nm on the substrate. Meanwhile, it's concluded that the thickness of Pd/Ag alloy membrane undergoes small variations with constant sputtering time.

At ambient temperature and pressure, the Pd/Ag alloy thin films with different thicknesses of 15.4 nm, 22.15 nm and 50.79 nm are used as sensing media to test the characteristics of optical fiber bundle hydrogen gas sensor in 4.1% standard hydrogen gas. The testing results recorded by Labview in real time are shown in Fig.3. We can see from Fig.3 that the amplitude response and the sensitivity of hydrogen gas sensor depend on the thickness of the Pd/Ag film. Comparing Fig.3(a) with Fig.3(b), it is shown that the thinner Pd/Ag alloy film can provide better sensitivity and shorter response time for hydrogen sensor. Nevertheless, the amplitude response of hydrogen gas sensor based on 15.4-nm-thick Pd/Ag alloy shown in Fig.3(a) is very small. At the same time, Fig.3(c) shows that the thicker Pd/Ag alloy film can provide better response amplitude but longer response time. The main reason is that the resultant PdH_x is hard to alter the morphology for thicker Pd/Ag alloy film, which finally retards the reflectivity changes of Pd/Ag alloy thin film. So after comprehensive consideration on response amplitude and response time, we note from Fig.3 that the hydrogen gas sensor based on Pd/Ag alloy thin film with thickness of

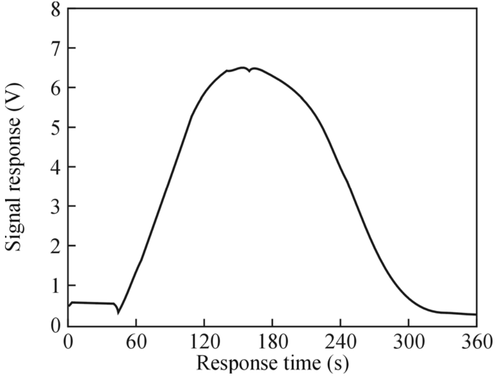
22.15 nm exhibits good amplitude response and fast response time, which is consistent with the theoretical result that the Pd/Ag alloy film with thickness of 20—30 nm is the best sensing medium for hydrogen gas sensor.



(a) 15.4 nm



(b) 22.15 nm



(c) 50.79 nm

Fig.3 Experimental amplitude response versus response time for three Pd/Ag film samples with different thin film thicknesses under normal conditions

In further hydrogen switch-on and switch-off tests, the optical hydrogen gas sensor responses were also recorded for 3.99% hydrogen at room temperature. It can be seen from Fig.4 that the output peak and the zero point can reach almost the same value in the three cycles, and the response rate and recovery rate of the hydrogen gas sensor are almost the same in the three cycles, so the hydrogen gas sensor demonstrates high reliability.

Fig.5 shows the morphologies of Pd/Ag alloy membranes, which were prepared by sputtering for 10 min at different substrate temperatures of 300 K, 473 K and 673 K under the constant sputtering power of 10 W. Three samples were measured on the Veeco NanoScope Multimode scanning probe microscope. The scanning electron microscope (SEM) images show that the surface roughness of Pd/Ag thin film is less than 1 nm. When the substrate temperatures are 300 K, 473 K and 673 K, the root-mean-square (*RMS*) roughness values of Pd/Ag alloy films are 0.622 nm, 0.452 nm and 0.423 nm, respectively. It is concluded that the higher the substrate temperature, the better the surface roughness of the Pd/Ag ultra-thin membranes. The increased temperature can raise the uniformity and compactness of Pd/Ag alloy and enhance the membrane reflectivity for hydrogen gas sensor. However, beyond a certain temperature (about 673 K), the Pd/Ag alloy surface presents rather large residual tensile stress, and defects may be generated during cooling the Pd/Ag film to ambient, which affects the lifetime of the sensing medium for hydrogen senor. So the substrate temperature of 673 K is adopted to reinforce the Pd/Ag reflectivity and stability.

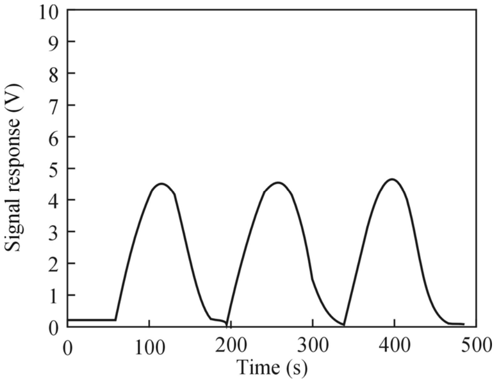
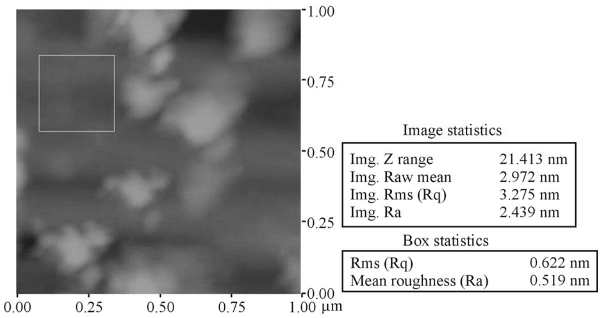
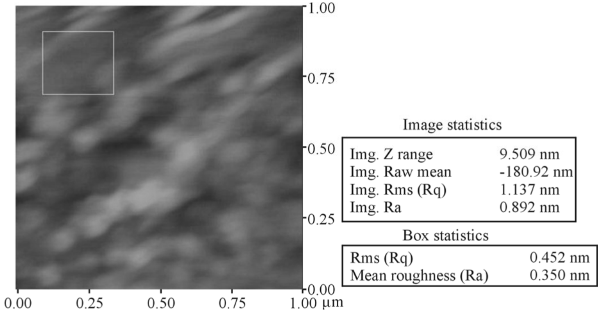


Fig.4 Reliability measurement for 3.99% hydrogen at ambient temperature and normal pressure

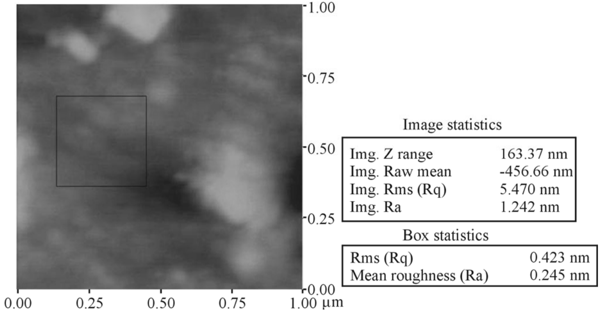
An optical microscope was used to capture the surface morphology images of the films while they were exposed in dry and humidified air. Compared with the two results in Fig.6, it's clear that under the humidity atmosphere, there are some white blisters in the SEM image. The formation of blisters alters the surface roughness of Pd/Ag alloy film on the glass substrates, which leads to the decrease of light reflectivity and the increase of transmissivity. At the same time, it's interesting to note that once the humidity is decreased, the image can reverse to the image in dry air as shown in Fig.6(b). The increased temperature can accelerate the evaporation of H_2O molecule from the Pd/Ag alloy, and thus reduces the humidity effect. The metal Ru or yttria-stabilized zirconia thin film is another potential approach for reducing humidity effects. It is likely that increasing the thickness of Ru buffer layer may further reduce the blistering effect, as reported in Ref.[11] using a thick Pt film as a buffer layer.



(a) 300 K

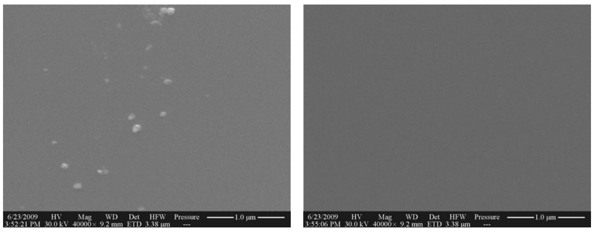


(b) 473 K



(c) 673 K

Fig.5 SEM images of the Pd/Ag alloy membranes prepared by sputtering for 10 min under 10 W plasma power at different substrate temperatures



(a) Humid (b) Dry

Fig.6 Optical microscope images of Pd/Ag thin films in humid and dry air

In the paper, we demonstrate a novel reflective optical fiber hydrogen gas sensor based on Pd/Ag binary alloy. The Pd/Ag alloy can eliminate hydrogen embrittlement in hydrogen gas sensor based on pure Pd. We summarize the optimum deposition time and substrate temperature for Pd/Ag alloy membranes prepared by DC magnetron sputtering. The humidity effect is analyzed, and some approaches are proposed to reduce it effectively. Although the optical fiber hydrogen gas sensor based on Pd/Ag alloy has been put forward, there is still some space for further improvement. First of all, the reduction of Pd/Ag alloy area could shorten the response time of optical fiber hydrogen gas sensor. Secondly, there are many other Pd-alloys which can be used as sensing media for hydrogen gas sensor. Pd/Yt alloy[12] has better hydrogen absorption, and it could improve the sensor selective sensitivity and shorten response time. But at present, the preparation of Pd/Yt thin alloy ultra-thin film is very difficult for optical fiber hydrogen gas sensor with modern technology.

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