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Study on deposition technique and properties of Pd/Ag alloy film sensor supported on ceramic substrate

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Abstract. Developing high-quality hydrogen sensitive material is the core part of hydrogen sensor, whose performance is determined by the sensitive response, reproducibility and recovery of hydrogen material etc. In order to overcome the defects of hydrogen embrittlement in previous hydrogen sensor which were based on the pure palladium, sliver as the second component added to the palladium was studied. Using photochemical etching technology to produce a bent metal mask, the mask is put on the ceramic substrate. Firstly, the thin film of Ta_2O_5 as a transition layer grew on the ceramic substrate. Then, a series of Pd/Ag alloy film sensors were prepared, and each performance characterization of Pd/Ag alloy film was studied. Testing results indicated that the thin film had a good linear output performance at 0~30% hydrogen concentration range, and demonstrates a high responsiveness and good repeatability. With temperature increasing, the strength of the responsive signal of the Pd/Ag alloy film decreases and its responsive time was also shortened.

1. Introduction

Developing high-quality hydrogen sensitive material is the core part of hydrogen sensor, whose performance is determined by the sensitive response, reproducibility and recovery of hydrogen material [1]. In order to overcome the defects of hydrogen embrittlement in previous hydrogen sensor which were based on the pure palladium, sliver as the second component added to the palladium was studied [2]. Pd/Ag alloy has good selectivity and permeability on hydrogen at room temperature. Therefore, the Pd/Ag alloy has become an important source of hydrogen sensitive material for hydrogen sensor. BaBaK had done a lot of research on the hydrogen sensitivity properties of palladium alloy system, such as the change of the electrical properties of Pd/Ni, Pd/Au, Pd/Ag and other alloys with hydrogen concentration [3]. Encountered hydrogen containing environments, the Pd/Ag alloy materials will form the palladium hydrogen structure which results in the electrical and optical properties changes of hydrogen sensitive materials. So, when the hydrogen concentration changes, the detection signal of Pd/Ag alloy is also changed.

In this paper, a thin film hydrogen sensor was designed and prepared by using Pd/Ag alloy as hydrogen sensitive material, and its sensing properties were tested.

2. Experimental

2.1. The working principle of hydrogen sensor

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Gas sensitive material is the key to gas sensor. There are different sensing properties and detection principles in gas sensitive materials. Hydrogen sensor detection principle is based on physical or chemical property change of gas sensitive material after the adsorption of hydrogen. Gas sensitive material of traditional hydrogen sensor is palladium or palladium alloy. When palladium was exposed to hydrogen environment, palladium hydrogen compound (Pd-H) was formed after palladium film had contacted with hydrogen. When palladium was from hydrogen, hydrogen molecules could strip from the metal palladium, the conductivity and many other features of palladium were back to the original form. Therefore, reaction of palladium with hydrogen is a reversible process. Working principle diagram of palladium alloy hydrogen sensor is shown in Fig.1 for the resistance measurement [4-6].

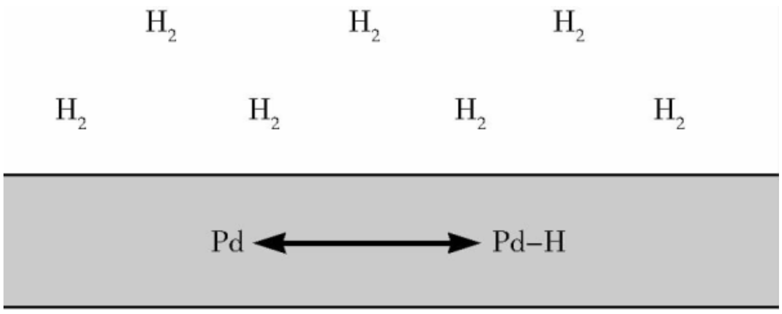

Figure.1 Palladium resistive hydrogen sensor operating principle

Due to limited range of pure palladium hydrogen storage, when the hydrogen concentration is high, the pure palladium will produce hydrogen embrittlement which leads off the film, and then the pure palladium hydrogen sensor fails. Adding silver to palladium will stabilize hydrogen palladium alloy, it can prevent the hydrogen compound phase transition from α to β phase. Pd/Ag alloy has good reversibility and rapid response capability at room temperature [7, 8]. Thus, at present, Pd/Ag alloy becomes an important source of the hydrogen gas sensor sensitive material.

2.2. Experiment methods

Pd/Ag alloy film preparation of Hydrogen sensor is prepared by the production of JGP-450B type magnetron sputtering deposition system. The Pd/Ag alloy coating process steps are as follows.

First, the alumina ceramic substrates were cleaned by absolute ethanol ultrasonic in 5min, washed with distilled water, and then dried.

Second, the metal masks were put on alumina ceramic substrates with the magnets below, and then the substrates were put into sputtering equipment. Pumping the vacuum to 5×10^{-4}Pa, the argon work pressure was adjusted to 0.5Pa. Next, the Ta_2O_5 transition layer was sputtered onto the substrate by selecting RF sputtering for 20s.

Last, pre sputtered Pd/Ag alloy for about 10min by using DC magnetron deposition, then Pd/Ag alloy film was sputtered on alumina ceramic substrate for 35s. After the Pd/Ag alloy sputtering well, the samples were annealed in argon gas atmosphere for one hour, and the annealing temperature was kept at 450 C.

3. Results and discussion

3.1. Relationship between film thickness and the resistance value

Five Pd/Ag alloy thin film sensors were obtained by magnetron sputtering at different sputtering time, as shown in Fig.2. Then the thickness of the Pd/Ag alloy film on alumina ceramic substrate was measured with the American XP-1 AMBIOS surface probe scanning step instrument. The film resistance was measured by the universal meter. The results of the measurement were shown in table1.

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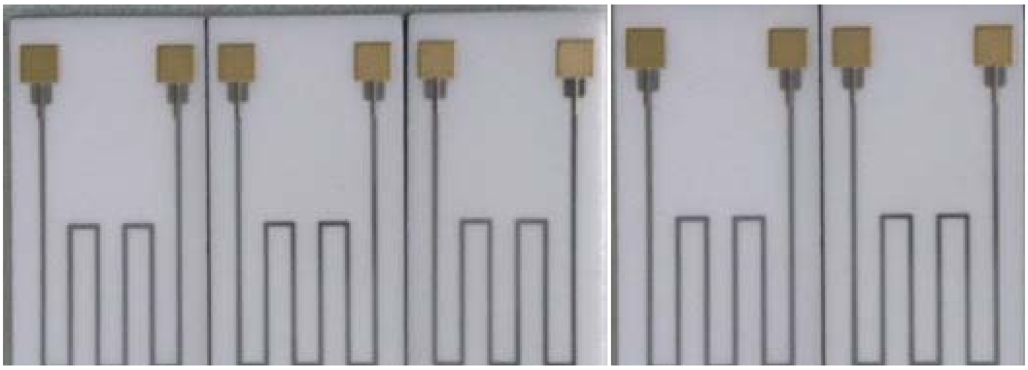

Figure2. Pd/Ag alloy thin film hydrogen sensors

Table1. Pd/Ag alloy membrane thickness and the resistance value

Sputtering time(s)	Resistance value(KΩ)	Film thickness(nm)
20	28.4	50
30	24.2	100
45	22.0	200
60	12.8	250
90	9.0	300

Pd/Ag alloy film resistance can be reduced with the increase of sputtering time, while Pd/Ag alloy film thickness increases. The Pd/Ag alloy film thickness is proportional to the sputtering time, and the resistance is inversely proportional to the film thickness.

3.2. Test of Pd/Ag alloy membrane response characteristic

Using three groups of different thickness of Pd/Ag alloy film as the hydrogen sensor sensitive material, hydrogen sensor amplitude and response time impacted by alloy membrane thickness were tested. Under the normal temperature and atmospheric pressure, 30% standard hydrogen gas was bubbled into three groups Pd/Ag alloy samples for 10 minutes, and then high purity nitrogen as the dehydrogenation was put into the container. In this process, the amplitude and response time of the sensors with different film thickness were recorded, the best film thickness range for Pd/Ag alloy hydrogen sensor was verified by comparing the results. Fig.3 shows the experimental results of hydrogen sensor output recorded in real-time by testing software.

- For the Pd/Ag alloy sensor with thin film thickness (less than 50nm), its response time for hydrogen is relatively fast, but its response amplitude is low, and the absorption of hydrogen is easy to reach saturation, as shown in Fig.3 (a)
- For the Pd/Ag alloy sensor with larger film thickness (more than 300nm), its response time of the hydrogen is relatively slow, and its response amplitude is low. It is shown in Fig.3 (c).
- For the hydrogen sensor with (100 ~ 300 nm) film thickness, as shown in Fig.3 (b), sensor performance is relatively stable and reproducible for 30% H_2. It can be seen from the figure that the response time of sensor is about 32s, and the hydrogen desorption time of the sensor is

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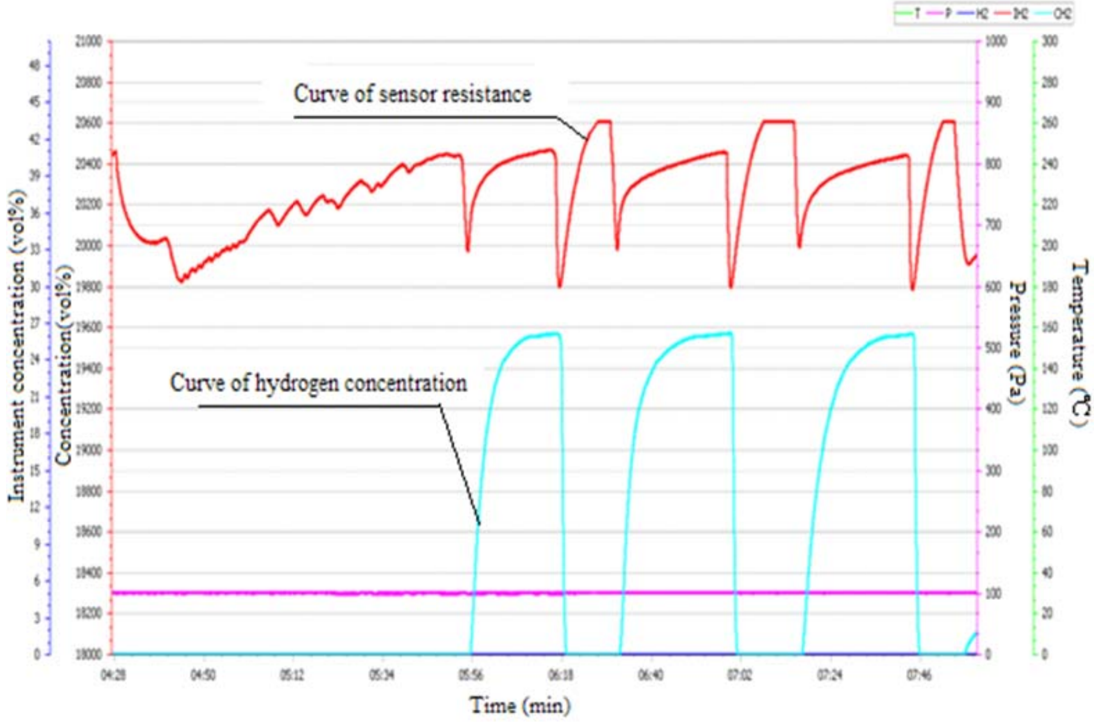
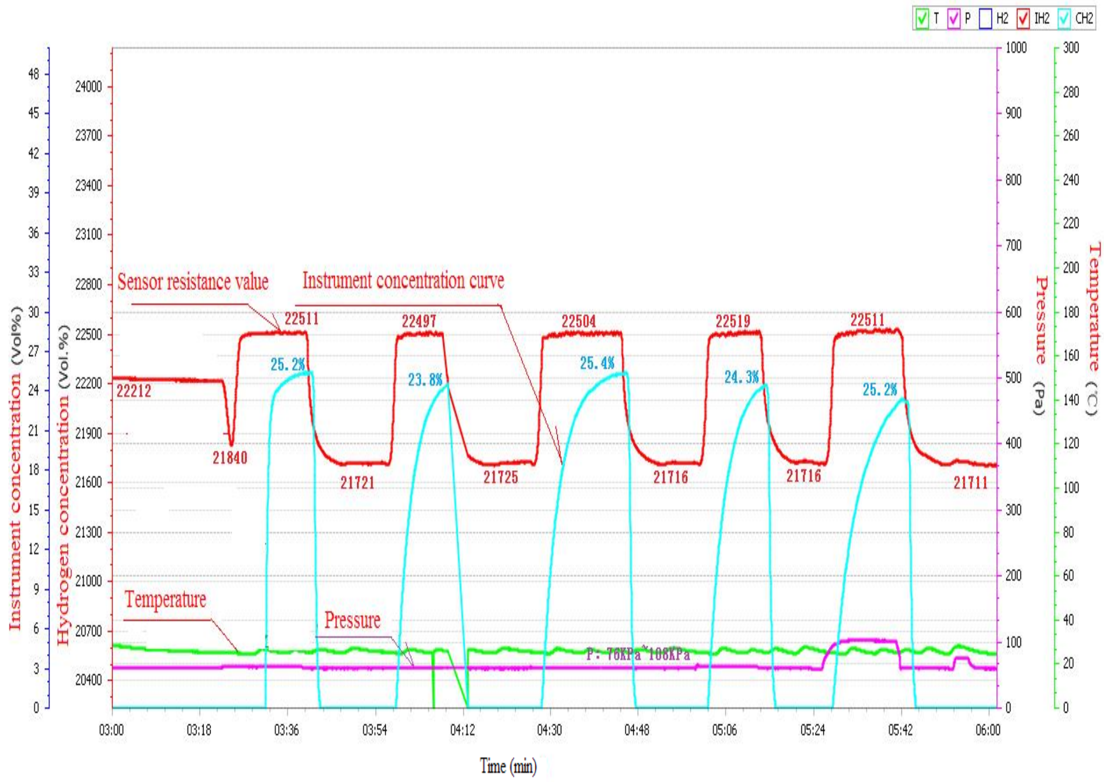
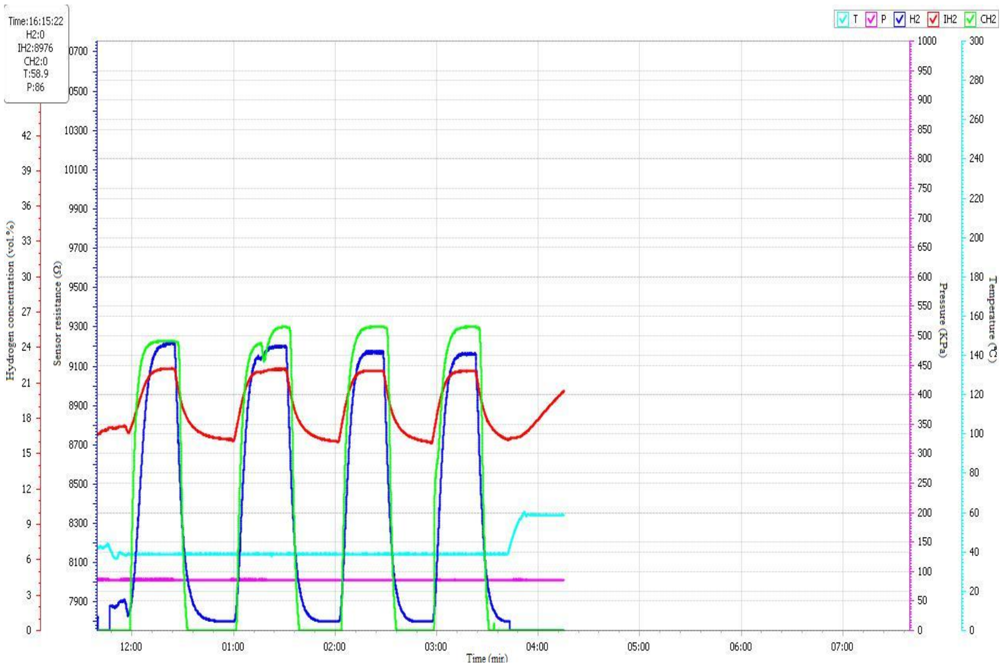
100s. Its response time is fast, and it is very suitable for reaction film as a hydrogen sensor.



(a) 50nm



(b) 200nm



(c) 300nm

Figure3. Response curve of different Pd/Ag alloy film thickness

3.3. Basal temperature effects on response performance

Pd/Ag alloy samples with different substrate temperature (200 ˚C, 300˚C, 450˚C) were passed into 30%H_2/N_2 standard gas in 10 mins, with high purity nitrogen as the dehydrogenation gas. Pd/Ag alloy films with different substrate temperature were compared with the hydrogen concentration response amplitude and response time, and then Pd/Ag alloy hydrogen sensor optimum substrate temperature was verified. Fig.4 shows the results of the hydrogen sensor output at different substrate temperature.

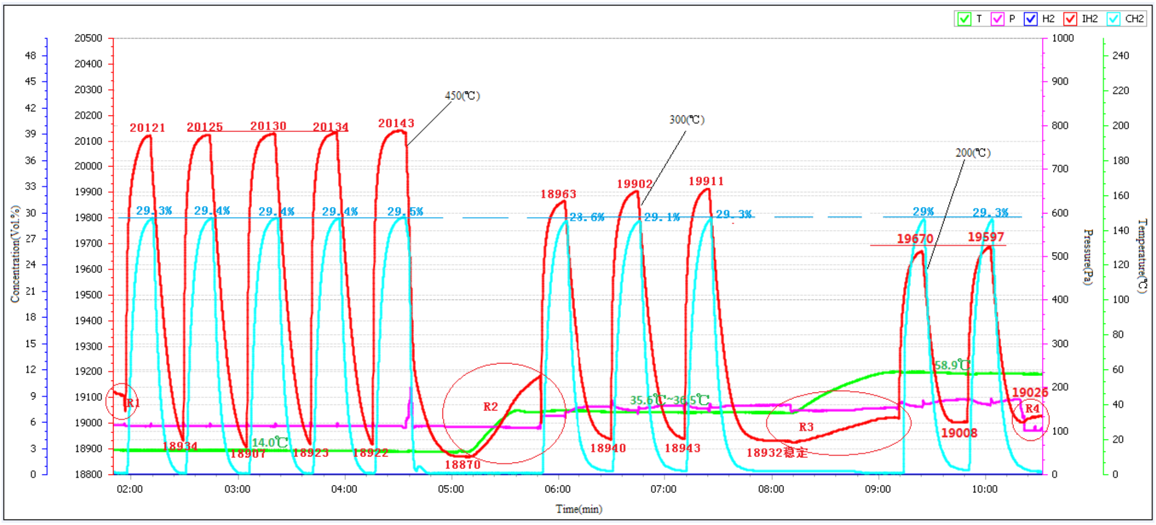


Figure4. Results of the hydrogen sensor output at different substrate temperature

The experimental results indicate that there are not many differences among the response time of the three kinds of samples, while the response amplitude is different, the higher the substrate temperature is, the higher the response amplitude is, the better the response is.

4. Conclusion

Pd/Ag alloy has good selectivity and permeability on hydrogen. Pd/Ag alloy system was selected as hydrogen sensitive material, and the film hydrogen sensors were prepared by using magnetron sputtering technology.

- The test results show that Pd/Ag alloy film resistance value is inversely proportional to the thin film thickness.
- The result of experiments shows that the sensor output signal has a good liner relationship in 0~30% hydrogen concentration. The sensor has high sensitivity, and its response time is about 32s, and the recovery time is about 100s.
- The experimental results indicate that there are not many differences among the response time of the three kinds of samples, while the response amplitude is different, the higher the substrate temperature is, the higher the response amplitude is, and the better the stability is.

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