An optical fiber hydrogen sensor with Pd/Ag film*

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A 20 nanometer palladium-silver (Pd/Ag) ultra-thin film was used for hydrogen gas sensing. The atomic ratio of Pd: Ag was 3:1, the thin film was evaporated on the optical glass, the Pd/Ag alloy could increase the life and provide the stability of the sensing film. The artificial neutral network was used for processing the data collected from the optical fiber bundle hydrogen sensor, which could enhance the measuring accuracy, at the same time, the intrinsic and extrinsic influences were eliminated mainly. Experimental results and numerical simulation show the training method available, a linear precision of 0. 1% for the optical hydrogen sensor is achieved.

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Hydrogen gas detection in different measuring environments has recently become a very important problem[1], lots of efforts have been made to develop high-performance hydrogen sensors with safety and longer life, optical sensors and especially fiber optic sensor technology provide opportunities for applications of optical sensors. Most of the optical fiber sensors use palladium (Pd) film as transducer to detect the concentration of hydrogen. Nonetheless, 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 morphology of pure palladium undergoes the $\alpha \rightarrow \beta$ phase transformations, and the process is irreversible. After several cycle of exposure to hydrogen, the palladium breaks off from the substrate. So in order to overcome the problem, a great of experiment reports introduce other metals to form palladium alloy. The Pd/Ag alloy could overcome the problem of hydrogen embrittlement. So far, Pd/Ag is perhaps the mostly studied alloy for hydrogen sensing[1]. Wang Min fabricated a zigzag-shaped microstructure of Pd-Ag plated on alumina substrate, the sensing performance of the mixed metal film is much better than that of pure palladium film[2]. In this paper we adopt 20 nm $Pd_{75}Ag_{25}$ ultrathin films evaporated on the float glass substrates in the optical fiber bundle sensor to overcome the well-known problem of hydrogen embrittlement.

The optical fiber sensor is affected by the intrinsic and extrinsic influences, so the optical hydrogen sensor has the characteristics of non-linearization in the whole output process. The paper presents a key technology—artificial neural network (ANN) to process the output signal from the sensor probe, ANN enhances the detection accuracy and adjusts the output non-linearity in the 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 adjustable substrate stage(with heating capability up to 400 °C) . Fig.1 is a schematic representation of the magnetron sputtering deposition unit. Before actual deposition, pre-sputtering is done

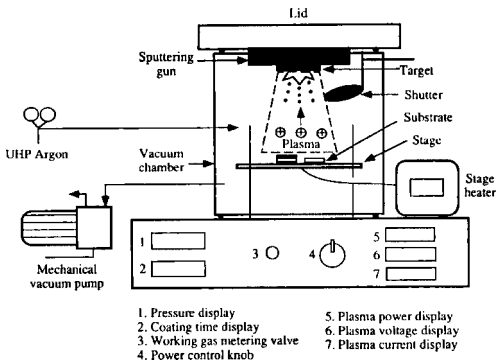

Fig.1 Schematic representation of magnetron sputtering deposition system

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for several minutes by masking the substrate. The step is necessary to stabilize the plasma power at the desired value before actual deposition starts. Tab.1 gives the key experiment parameters for dc magnetron sputtering. In Tab.1 different sputtering time depends on the dc sputtering power, under the fixed the sputtering power, the thickness of film lies on the sputtering time.

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 schematics of the sensor testing station. The performances of optical fiber hydrogen sensor are tested with the experiment setup which is made up of several parts: 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 transimpedance preamplifier circuit with a responsivity of 5 mV/μW. According to the parameters in Tab.1, the 20 nanometer $Pd_{75}Ag_{25}$ thin films are evaporated on the optical glass substrates in vacuum as the hydrogen sensing film. The hydrogen mixing and adjusting apparatus help to achieve the baseline and realize the constant gas input; the gas chamber is composed of two separated gas cell like Fig.2. One of the gas cells is considered as the reference cell in the experiment, 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 fiber to form the coaxial optical fiber bundle. The fibers in the central of the sensor are transmitting fibers, the others are receiving fibers.

In the paper of M.A.Buelter[3], the useful reflective light was very weak, most of light from light source transmitted through the palladium film and lost. Compared with the model brought forward by M.A.Buelter, the novel reflective optical fiber bundle hydrogen sensor provides high density of reflective light which contains the information of hydrogen concentration, and it's convenient for the subsequent signal-processing.

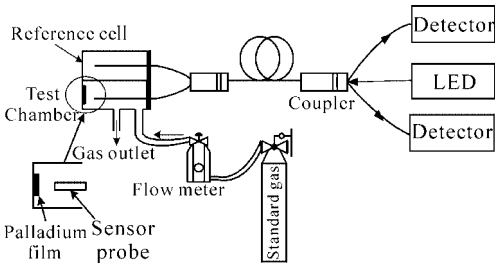

Fig.2 Experimental setup for optical fiber bundle hydrogen sensor

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

$$V_1 = K_1 G_1 R \delta_1 P_0 f(d_1) \text{ and } V_2 = K_2 G_2 R \delta_2 P_0 f(d_2) \ , \quad (1)$$

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, d_i is the reflective distance from the sensor probe to reflective surface, the receiving fibers could receive maximum light density for the coaxial optical sensor probe when $d_1 = d_2 = 1$ mm, the function $f(\bullet)$ is the modulation characteristic function of the suface, the receiving fibers conld receive maximum light density for optical fiber bundle[4], then the ratio of the two receiving signals is obtained as equation (2), dimensionless parameter Γ represents the concentration of hydrogen.

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

where δ_1 changes along with the hydrogen concentration when palladium exposure to the hydrogen, G_1, G_2, $f(d_1)$, $f(d_2)$ and δ_2 are constants in equation.

Assuming that the model of the sensor system can be expressed as the following eq.(3)

$$(V_1, V_2) = f(\Gamma, n) \ , \quad (3)$$

where n is the interference coefficient in hydrogen sensor, Γ is the concentration of hydrogen, V_1 and V_2 are the sensor actual output, and $f(\bullet)$ is an uncertain non-linear function. Through the equation above, we can get

$$\Gamma = f^{-1}(V_1, V_2, n) \ . \quad (4)$$

In eq.(4), $f^{-1}(\bullet)$ is also an uncertain inverse non-linear

function of $f(\bullet)$. So the ANN could take V_1 and V_2 as its two inputs, and Γ as its output. So the principle of training by neural network is presented as shown in Fig.3.

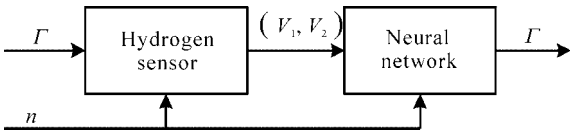

Fig.3 Principle of training by neural work

The theorem of Hecht-Nielsen has been proved that when given that the sum of square $\varepsilon > 0$, an artificial neural network (ANN) of three layers can approach any continuous nonlinear function[5,6]. Furthermore, ANN has the function of generalization. And we could utilize the characteristics to build a back propagation (BP) network. The architecture of BP is shown in the following Fig.4; the neuron numbers of input-layer and output-layer are 2 and 1 in the BP neural network, respectively; the input activation function is set to logarithm transfer function $f(x) = \log sig(x)$ and the output activation function is set to linear transfer function $g(x) = purelin(x)$.

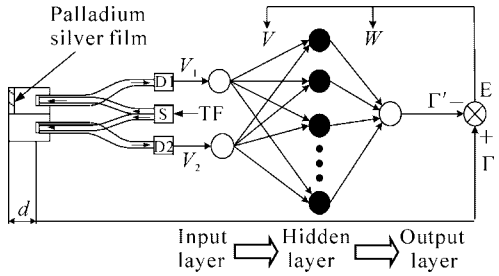

Fig.4 Structure of BP artificial neural network

In Fig.4, d is reflective displacement of hydrogen sensor in experiment and d=1 mm; V_1 and V_2 received from two detectors in optical fiber bundle probe are the two power values in the input layers; on the other end of the ANN, in eq. (5) we could obtain the hydrogen concentration Γ'; E is error function in eq.(6); h is the hidden neurons of the BP network in eq.(5) and eq.(7); w and v are weight vector and thresholds of the neural network module in eq.(7), w and v are matrixes, during the process of training, w and v are updated continually in BP neural network.

$$\Gamma' = g\left[\sum_{j=1}^{h} w_j f\left(\sum_{i=1}^{2} v_{ij} F_i\right)\right], \tag{5}$$

$$E = \sum_{k=1}^{m}\left[\Gamma(k) - \Gamma'(k)\right]^2, \tag{6}$$

$$E = \sum_{k=1}^{m}\left\{\Gamma(k) - g\left[\sum_{j=1}^{h} w_{jk} f\left(\sum_{i=1}^{2} v_{ij} F_i\right)\right]\right\}^2. \tag{7}$$

In eq.(6) and eq.(7), the coefficient m is the sum of sampled-data. With the decrease of difference between E and ε, Γ' is becoming more and more close to Γ, that is to say, Γ equals to Γ' approximately. So through ANN shown as Fig.4, the way of data-processing eliminates the interference factors, and adjusts the non-linearization better in optical fiber reflective hydrogen sensor.

The structure of the neural network is easy, the process of arithmetic using BP neural network is also simple. In the program of the BP neural network, we choose the training 5000 times, the training output goal $\varepsilon = 0.001$.

During the process of the experiment, we collect 5 sample points in V_1 and V_2, in other words, the coefficient m equals to 5 in the eq.(6) and eq.(7). The measurement data of the optical fiber bundle hydrogen sensor are listed in Tab.2.

Tab.2 Result of testing values of the hydrogen sensor (Unit: %)

Number	Sensor output V_1 (Unit: V)	Sensor output V_2 (Unit: V)	Calibration output Γ	ANN output Γ'
1	2.0246	2.6235	0.00	-0.0039
2	1.9852	2.6254	1.00	0.9994
3	1.9268	2.6263	2.54	2.5391
4	1.9232	2.6263	2.99	2.9889
5	1.8896	2.6235	3.99	3.9899

In order to obtain the optimizing results and the minimal training error of hydrogen sensor through the BP network, it is required to choose the appropriate hidden neurons and training function for BP network. The BP network which has different hidden neurons is provided with different network errors as in Tab.3.

Tab.3 Result of training errors of the hydrogen sensor based on BP network

BP Hidden neurons	Training function of BP		
	traingdx	trainlm	traingd
3	0.1856	0.0274	0.1967
4	0.1718	0.0704	0.1493
5	0.9490	0.0694	0.3150
6	0.0707	0.0694	0.1368
7	0.0704	0.0665	0.1732
8	0.0706	0.0031	0.3070

Tab.3 shows that the BP network achieves the minimal training error when hidden neurons are 8 and the training

function adopts the training function—trainlm. So the *h* equals to 8 in eq.(5) and eq.(7).

Fig.5 shows that the output hydrogen concentration Γ' is almost on the same line. Compared with the fitting-line, the result after training by BP neural network will be better in the linearity.

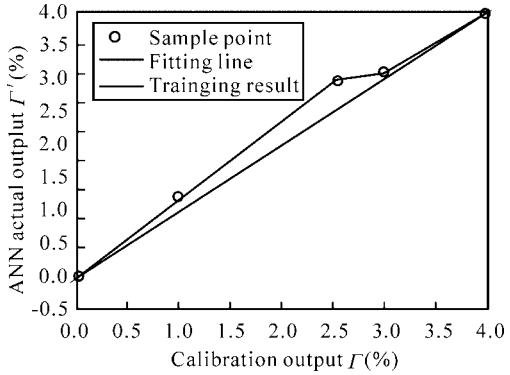

Fig.5 Fitting-line and the BP neural network output hydrogen concentration Γ'

For ultrathin films the dc Sputtering has several advantages like: (a) synthesis of ultrathin films with minimal impurity; (b) easily controllable process parameters; (c) flexibility for synthesizing alloys; and (d) the ability to generate nanostructured films. The optical fiber bundle hydrogen sensor based on the artificial neural network has the characteristics of more accuracy and better linearity. The result indicates that this hydrogen measurement system has a good linearity, and the achieved precision is 0.1%. It will be suitable for the application in data-processing of all kinds of optical fiber sensors to eliminate the interferences, it possesses a high applied value.

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