Conference Paper

Sensor Explosive Concentrations of Hydrogen

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Abstract

The article describes a resistive sensor explosive concentrations of hydrogen with a response time of about 0.1 s is completely selective for hydrogen.

1. Introduction

Hydrogen, as a technical product, is widely used in many industries, in technological processes of oil refining, ammonia production, methanol and metallurgical industry. Hydrogen is considered as a coolant and as an energy accumulator. Use of hydrogen as a fuel in vehicles is very promising. Environmentally friendly cars on hydrogen engines and rocket on oxygen–hydrogen fuel are already used. However, hydrogen has wide explosion limits (4–75%) and small ignition energy mixed with air (0.02 mega joule). Therefore, the task of creating reliable methods for monitoring hydrogen leakage at all stages from receipt to the application is relevant. Promising is the development and use of systems based on solid-state sensors. They allow you to achieve the miniaturization, mechanical strength and work in real-time and low cost. This work is devoted to studying the performance and sensitivity of resistive sensor explosive concentrations of hydrogen.

2. Materials and Methods

Diagram of the sensor is shown in Figure 1. It represents an insulating substrate (4) coated with a thin film of palladium (5) and aluminum contacts (1) for measuring the electric resistance of the hydrogen-sensitive thin film. The sensor is heated by a resistive heater (2) via electrical contacts (3).

The sensor cell is manufactured with the help of laser technology for deposition of thin films. The film of palladium with a thickness of 20 nm was coated on a plate of glass ceramics 0.4 mm thick (sital) with help solid-state laser in a vacuum chamber. Before the coating plate was aged in a vacuum at a temperature of 350°C for three

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hours. Then, on the film of palladium with using the method of thermal spray deposited aluminum contacts [1].

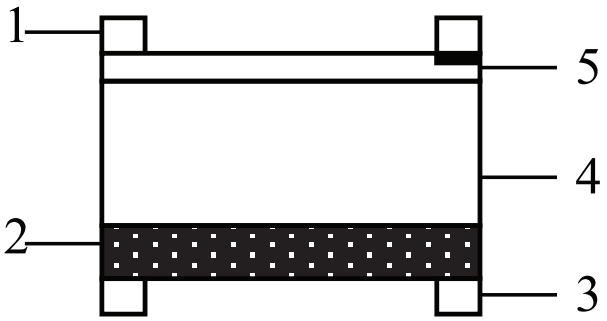

Figure 1: The scheme of the sensitive element (sensor) 1 – contacts for measuring the electrical resistance; 2 – thin film heater; 3 – contacts for current supply; 4 – insulating substrate; and 5 – palladium film.

After completing all the processes of spraying on the plate with help a diamond cutter, we cut the plate into individual samples with dimensions of 4 x 8 mm^2. The resistivity of the samples of the sensors was 150–200 Ω.

The arrangement work for the sensor was carried out as follows. A thin film of palladium is heated to a temperature of 400°C, while at the same time is measured by its resistivity. When the film resistance reaches 3–4 kΩ, the heater temperature decreases to 100–150°C. In this state, the sensor is ready for operation.

The principle of operation the sensor consists in the change of its electrical resistance when the concentration of hydrogen in the environment. The basis of this principle is the chemical reaction of reduction hydrogen-sensitive thin film oxide of palladium:

$$PdO + H_2 \rightarrow Pd + H_2O.$$

Figure 2 shows schematic curves showing sensor response to the appearance of hydrogen in air. Let at time t_1 (Figure 2(a)) into the air surrounding the sensor arises hydrogen concentration K_1 of the order of several percents. The electrical resistance of the sensor at first grows and then decreases rapidly (Figure 2(b)). The value of $K_1 \geq K_0$, where K_0 is the minimum (threshold) concentration of hydrogen in which the value of the electrical resistance of the sensor changes abruptly from the value R_1 to a value R_2 (at $K_1 < K_0$, the electrical resistance only increases slightly). The ratio R_1/R_2 can be set by the degree of oxidation, for example, two to three orders of magnitude.

If hydrogen concentration increases slowly (Figure 2(c)), the reaction time increases (Figure 2(d)), but when the gas concentration reaches K_0, the resistance of the sensor abruptly reduced to the value R_2.

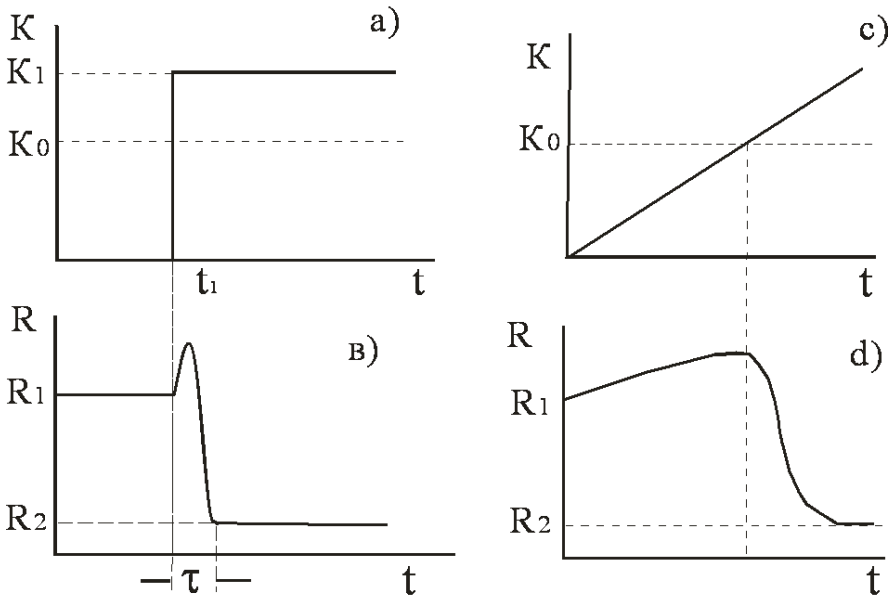

Figure 2: The principle of operation of the sensor: (a) dependence of the concentration, C, of hydrogen in air from the time t; (b) dependence of the electrical resistance, R, of the sensor from time to time; (c) with slowly increasing concentration; (d) is the corresponding curve and (c) the dependence of the electrical resistance of the sensor from time to time.

After deployment, the sensor can be re-moved from the state with low electrical resistance in a state with a high electrical resistance (the state of the oxide). For this, you need temporarily to increase the temperature to 300–400°C. While the palladium thin film again partially oxidized. In the oxidized state, it is again ready for the next work cycle. The sensor can withstand 5–7 cycles, after which hydrogen-sensitive film is destroyed.

3. Results

Figure 3 shows the dependence of the resistance of the sensor from the time when applying it to different concentrations of hydrogen. From dependences, it is seen that in the sensitive layer after exposure to hydrogen occurs two processes. One process leads to increased resistance of the sensitive film, the other to decrease. When the hydrogen concentration is small, goes only the first process (Figure 3(a)). It is identical to the processes occurring in the sensors based on oxide semiconductors [2].

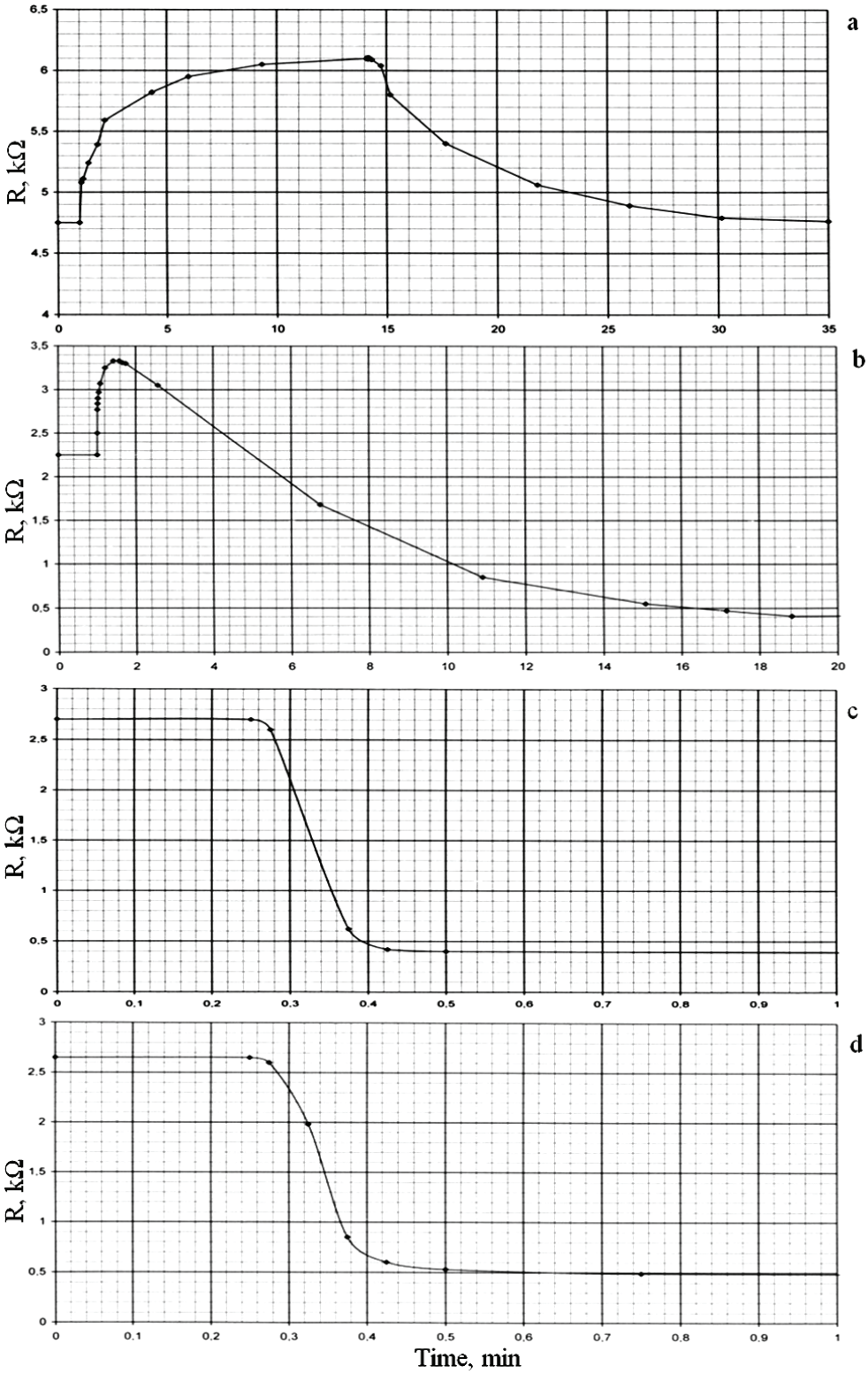

Figure 3: The sensor's dynamic characteristics. The concentration of H_2: (a) 200 ppm, (b) 2000 ppm,(c) 1 %, and (d) 4 %. The sensor's temperature is 100°C.

4. Discussion

With increasing hydrogen concentration, there is a sharp increase in the resistance and an increase in the amplitude of the response. When the hydrogen concentration is 1000 ppm, begins to show the second process, which results in a decrease in the resistance of the sensitive layer (Figure 3(b)). This process is associated with the restoration of the oxide film of palladium. When hydrogen concentrations are achieved close to 0.2 vol.% on a reducing reaction proceeds quite slowly (about 10 min, Figure 3(b)). With increasing hydrogen concentration up to 1 vol.% and more, the rate of reaction of recovery decreases significantly and is a fraction of a second (Figure 3(c), (d)).

The value of the threshold concentration K_0 is determined by the thickness of the oxide film and the temperature of the sensor: If there is a reduction in the film thickness of the oxide, the value of K_0 decreases, with increasing temperature the value of K_0 also decreases. Thus, by varying the thickness of the sensitive layer and the operating temperature, it is possible to change the value of K_0. The value of τ also depends on temperature: The higher the temperature, the smaller τ at a fixed hydrogen concentration.

5. Conclusions

It was studied the dependence of the initial resistance of the sensing layer from the storage time at a temperature of 20°C, and also prolonged furnace annealing at a temperature of 100°C. The measurements were carried out for three months and showed that the storage of the sensors as at room temperature so at a temperature of 100°C, the resistance of the sensors does not change.

The experiments showed that the response time of the sensor depends weakly on the composition of the gaseous environment in which the measured hydrogen concentration. The sensor can be used not only in the air but also in other gas media: nitrogen, helium, oxygen, hydrocarbons, inert gases, etc. Because the reduction reaction of the oxide required the presence of hydrogen, the sensor, thus, is selective toward H_2.

References

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