OPTICAL AND RESISTANCE SENSORS FOR HYDROGEN DETECTION IN GAS MIXTURE AND TRANSFORMER OIL

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Results of the investigation of thin Pd layers as hydrogen sensors are presented. Two types of sensors are examined - resistance and optical sensors. Changes in measured signal as a function of hydrogen concentration in hydrogen-nitrogen mixture are registered. The sensor is exposed either directly to the gas mixture or to the transformer oil, through which the gas mixture passes. The hydrogen concentration in the mixture changes from 0.5% to 4.0%. Investigated sensors are sensitive enough in this concentration range, in both media. Changes of Pd film properties caused by hydrogen absorption are reversible except a few first exposures to the mixture. Obtained results confirm the possibility of developing simple sensor for detection of hydrogen gas in dissolved in the transformer oil.

Keywords: hydrogen sensor, thin films, gas mixture, hydrogen dissolved in oil

1. INTRODUCTION

Rising interest in the development of hydrogen sensors is mainly caused by possible use of hydrogen as a fuel. Different types of such sensors are described in a review paper [1]. Most of them base on thin palladium layers as a catalyst. Palladium has high hydrogen solubility and is very selective to it. The absorption of hydrogen in Pd depends on temperature and hydrogen concentration. As a result of hydrogen absorption basic physical parameters of Pd change. The work function of Pd, which is normally 5.1 eV decreases due to hydrogen absorption by 0.7-1.0 eV.

Additionally film thickness increases. It causes changes to electrical and optical properties of palladium.

In the paper experimental results obtained for the sensors based on thin Pd films deposited on glass are presented. At the first stage the sensors are investigated in a gas atmosphere. But the main aim of the work is to develop sensors for the detection of hydrogen dissolved in the transformer oil.

The analysis of gases dissolved in the transformer oil is an accepted method for the early detection of incipient faults in power transformers is. The interpretation of the results of such an analysis is specified in IEC Publication [2]. The increase of hydrogen concentration testifies that partial discharges take place in the transformer. The authors intend to develop sensor for continuous monitoring of hydrogen concentration in oil, in power transformers and other electrical power plants.

2. SAMPLES AND METHODS

Thin Pd sensor films are deposited on glass substrates by evaporation in vacuum. Typical layer thickness is about a 15 nm. Two types of samples are prepared. For electrical measurements the film was deposited on glass plate with preliminary prepared electrical contacts (Fig. 1a). The second structure uses for simultaneous electrical and optical measurements is shown in Fig. 2b. Samples are placed in special chamber. Pure nitrogen or nitrogen-hydrogen mixture is fed to the chamber. A gas flux is constant and equal to a 1.00 l/min. A hydrogen concentration in the mixtures changed from 0.5 % to 4.0 % in volume. The mixture is fed for a 30 or 60 min. After each application of the mixture pure nitrogen was fed for a 60 min. For measurement in the transformer oil the chamber is filled with the oil. The mixture of nitrogen and hydrogen is inserted into transformer oil through a perforated tube, placed near the bottom of the cell.

a.

b.

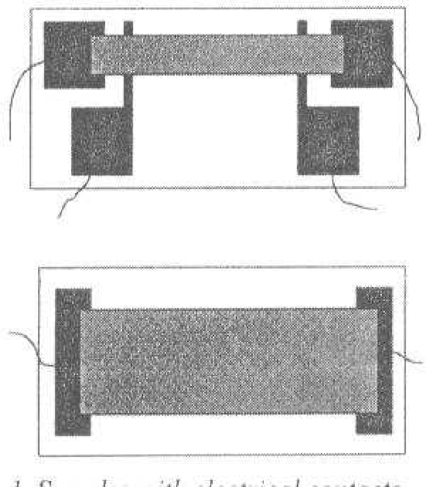

Fig. 1. Samples with electrical contacts for electrical (a.) and simultaneous electrical and optical measurements

Two types of experiments are carried out. The first type bases on ac measurements with lock-in signal detection. Configurations of measuring set-up for electrical and optical ac measurements are shown in Fig. 2a and 2b, respectively.

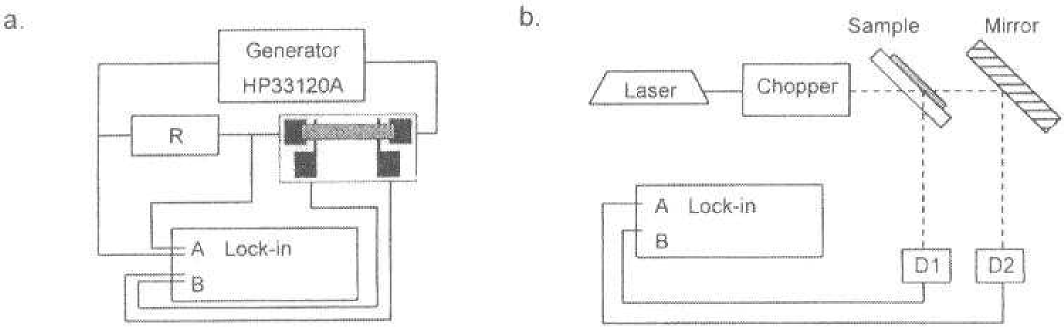

Fig. 2. Schemes of ac electrical (a.) and optical (b.) measurements

For electrical measurements an ac current from the signal generator (sine wave) is applied to the sample. Amplitudes of voltage drop on known resistor R and voltage on potential contacts of the sample are measured. From these two measurements the resistance of the film has been calculated.

For detection of changes to optical properties of the Pd film the sample is illuminated with intensity modulated laser beam. The intensity of beams reflected from the sample and the mirror are converted into electrical signal by photodiodes and measured by lock-in nanovoltmeter. In order to avoid influence of light beam intensity variation the ratio of these signals is calculated.

Simultaneous electrical and optical dc measurements are carried out using the experimental set-up shows in Fig. 3. The sensor is pressed down to a window of the measuring cell with the Pd film exposed to the oil. A thin layer of the immersion oil is applied between the sensor and the window for better optical contact. The electric resistance of the Pd film is directly measured using prepared contacts. Changes to the optical properties of the film are examined through the intensity of light reflected at the glass-film interface. A laser-diode emitting at 670 μm is used as a light source for the optical measurements. The intensity of the light reflected from the Pd film is monitored by the photoresistor (PhR1). Light from the laser is preliminary polarized. A polarization plane is selected so as to minimize the intensity of light reflected from the cell window. Additionally the light beam passes through a glass plate. The intensity of light reflected from this plate is measured using another photoresistor (PhR2). It makes it possible to take into account the influence of the instability of the light source during analysis of the reflection signal.

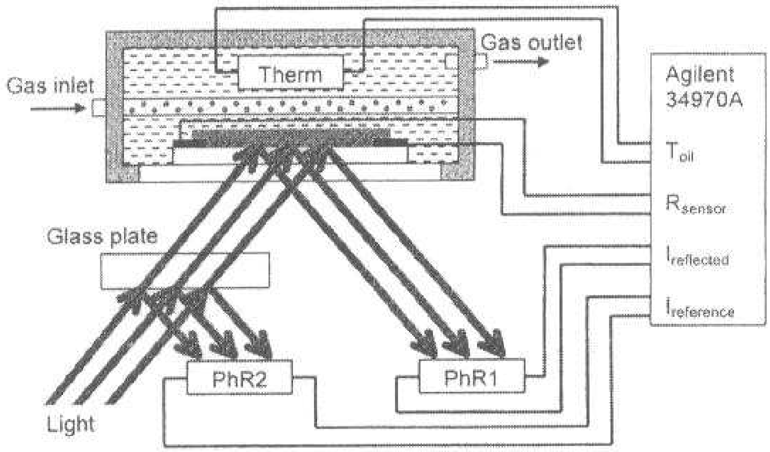

Fig. 3. Experimental set-up for simultaneous electrical and optical dc measurements

Measurements are carried out in the temperature range 20°C - 120°C.

3. RESULTS

Results of electrical ac measurements in the gas mixture are shown in Fig. 4. Changes of the hydrogen concentration in the mixture cause distinct changes to the film resistance. The resistance grows almost proportionally to the concentration. The situation is different for the first and the second exposition. After the first exposition considerable drop of the resistance is observed. Next exposition causes only small reaction of the film. Similar conclusions may be drawn from optical measurements. Transmittance of the film drops with increasing of hydrogen concentration. Unfortunately optical measurements are very noisy. A possible reason for it is unstable operation of a laser.

The dc measurements in the gas mixture are carried out for the same samples, so their behaviour during the first exposure to the hydrogen can not be examined. In this case the reflectivity of the film was determined. Both resistance and reflectivity of the film change with changes of hydrogen concentration (Fig. 5). The serious drawback of these measurements is a long-time drift of both registered signals.

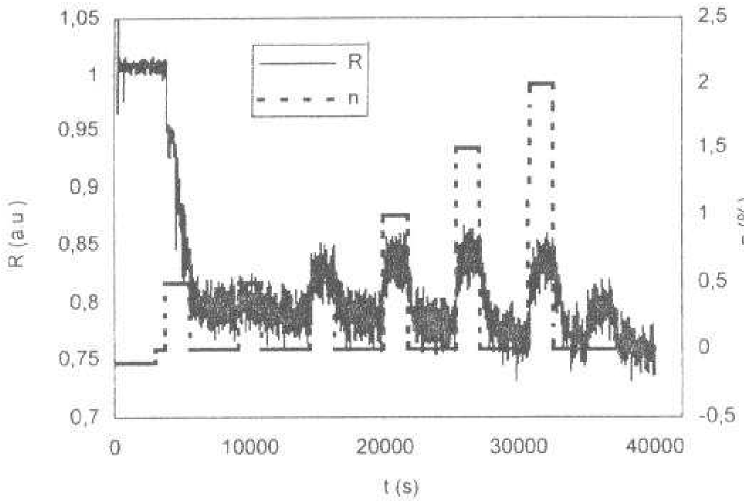

Fig. 4. Resistance of Pd film measured by ac method (solid line) and concentration of hydrogen in hydrogen-nitrogen mixture (dotted line)

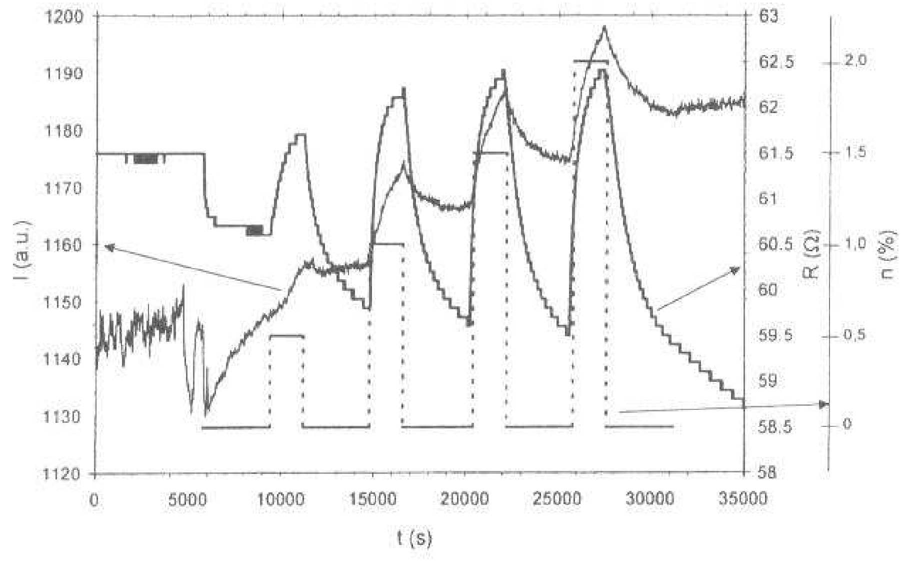

Fig. 5. Changes in the resistance and the reflectivity of Pd film caused by the hydrogen absorption and measured by dc method

This long-time drift may be corrected using numerical methods. In Fig. 6 corrected dependencies of the resistance and the reflectance of the film on time are shown. One can see that these changes strongly depend on the hydrogen concentration in the gas mixture

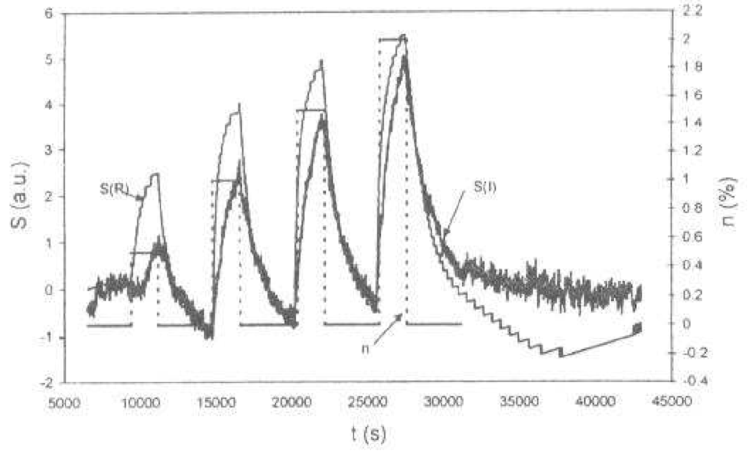

Fig. 6. Changes in the resistance and the reflectivity of Pd film caused by hydrogen absorption after correction for long-time drift

The next stage of the investigation is the examination of developed sensor structures in the transformer oil. Measurements are carried out at 20°C (room temperature), 50°C, 85°C and 120°C. The last temperature is higher than normal operational temperature, but at such high temperature aging effects are more significant. Obtained results are very similar to these for the measurements in gases. Typical measured resistant and reflectance signals are shown in Fig. 7.

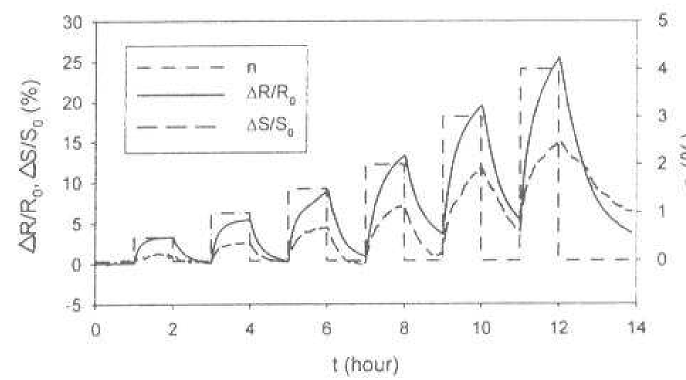

Fig. 7. Relative changes of Pd film resistance (solid line) and reflectance (doshed line) caused by hydrogen dissolved in the transformer oil

Practically interesting results are obtained from comparison of the dependencies measured at different temperatures. As it is shown in Fig. 8, the temperature rise causes the drop in the sensor sensitivity and the sensor reaction time. The first effect may lead to problems with interpretation of signals measured at different temperatures.

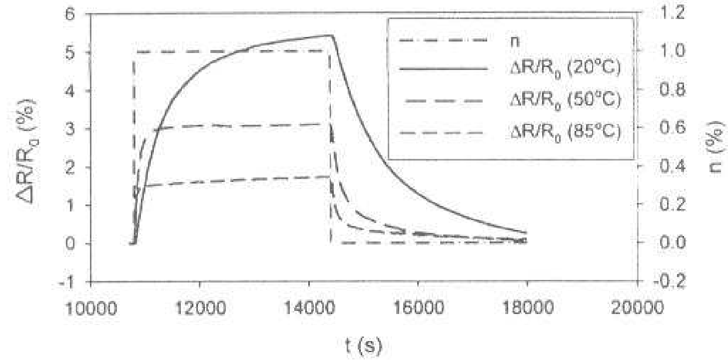

Fig. 8. The resistance sensor answers measured at different temperatures of the transformer oil

4. CONCLUSIONS

Obtained results confirm the possibility use thin Pd films as the active layer in hydrogen sensors for operation both in gaseous and liquid media. Two types of sensors are examined – the electrical (resistance) sensor and the optical one. Both sensors have sufficient sensitivity in considered range of hydrogen concentration. The measured changes are reversible, except the first few exposure to hydrogen. The signal to noise ratio is much better for electrical sensor, but the optical one is more insensitive to electromagnetic interferences. This is especially important for applications in electrical power plants. The main problem, which must be solved, is the long-time stability of the sensors. Preliminary experiments have been carried out with sensors covered by additional protective layer. Application of this layer significantly improves the sensor stability, but at the same time causes decrease in its sensitivity.

Also the problem of the sensitivity dependence on temperature should be considered. Possible solutions are the stabilization of the sensor temperature or the use of correction curves.

The hydrogen sensors proposed in this paper have very a simple structure and demonstrate high sensitivity to hydrogen either in the gas mixture or dissolved in transformer oil. It would seem to be possible to use such a sensor for the continuous monitoring of power transformers and other electrical power systems.

ACKNOWLEDGEMENTS

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