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Comparison of Field Effect Transistor with C-nPd gate and resistive C-nPd film sensing properties toward hydrogen

Abstract. *As a result of the implementation of the POIG project (UDI-POiG.01.03.01-14-071/08-00), the research network Łukasiewicz, the Tele- and Radio Institute and the Warsaw University of Technology, developed resistance hydrogen sensors using changes in nanocomposite resistance. Carbon-Palladium films (C-nPd) were obtained by PVD method, followed by transistor sensors (FET) with a gate covered with a previously developed nanocomposite C-nPd film. In this article, we show differences in a sensing properties and reaction of discussed resistance for the transistor sensors with a C-nPd film and resistive sensors built of C-nPd film deposited on ceramic substrate. For both types of sensors we performed sensing characterization in a research set-up prepared especially for this purpose during the implementation of the project. We found that transistor sensor is much more sensitive toward hydrogen than resistive sensor.*

Streszczenie. *W wyniku realizacji projektu POIG (UDA-POIG.01.03.01-14-071/08-00) realizowanego w latach 2009-2015 . Sieć Badawcza Łukasiewicz Instytut Tele- i Radiotechniczny oraz Politechnika Warszawską opracowały oporowe sensory wodoru wykorzystujący zmiany rezystancji nanokompozytowych warstw węglowo-palladowych (C-nPd) otrzymywanych metodą PVD, a następnie sensory tranzystorowe (FET) z bramką wykonaną z opracowanej wcześniej nanokompozytowej warstwy C-nPd. W tym artykule zostały pokazane różnice we właściwościach sensorycznych i ich reakcjach na wodór dla obu typów sensorów tranzystorowego i oporowego w postaci warstwy C-nPd osadzonej na podłożu ceramicznym. Dla obu typów sensorów badania sensorowe były prowadzone na specjalnie do tego celu zbudowanym stanowisku badawczym.(* ***Porównanie możliwości detekcji wodoru przez tranzystor polowy z bramką C-nPd oraz warstwę rezystancyjną C-nPd)***

Keywords: hydrogen sensors, thin layers, resistance measurement, C-nPd film
Słowa kluczowe: sensory wodoru, cienkie warstwy, pomiary rezystancji, warstwy C-nPd .

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Introduction

Efforts to reduce CO2 emissions are heading towards searching for new environment -friendly energy carriers. One of the most important candidates for such an energy carrier is hydrogen. Despite numerous advantages in the direction of collecting and storing, hydrogen also has disadvantages such as very high volatility and a relatively low explosion threshold (4% concentration in the air). The consequence of the threats that brings the possibility of a mixture of explosive air with hydrogen is the need to monitor hydrogen concentration near transmission and storage installations. FET transistor gas sensors have been attracting much attention because they can be miniaturized and applied to the Internet of Things (IoTs) [1]. The resistor-type gas sensors and FET-type gas sensors detect gas through changes in the conductivity of the sensing material and the threshold voltage of the FET, respectively. The size of the resistor-type sensor is larger than FET with nanostructured sensing materials as a gate material. The increase of response of such transistor device is easy while response of resistor with the same nanostructural material used as resistor is stable. As the size of the resistive sensor increases, the power consumption of the sensor increases, especially when resistor needs a heater. On the other hand some authors found that the response of Si FET-type gas sensors has been lower than that of the resistor-type gas sensors [2-4].

In our group, we elaborated FET and resistive sensor based on nanocomposite carbonaceous-palladium film (C-nPd film). The C-nPd film is composed of nanometer in size grains of palladium placed in carbonaceous matrix. The structural form of this matrix is graphene-like and it consists of small graphene domains of few tens of nanometers in size [5 - 8]. The absorption/desorption process of hydrogen is reversible and it does need a heater to reverse the process of absorption.

In this paper, we compare the response characteristics of a field-effect transistor (FET)-type with C-nPd film as the gate and resistive C-nPd film on allundum substrate hydrogen sensors. Experimental results shows that FET/C-nPd sensors have better properties toward sensing hydrogen than sensors based only on C-nPd films. On the other hand, FET/C-nPd sensors are more complicated in production and expensive.

Experimental

The C-nPd film is obtain with PVD method described elsewhere [9]. Such film can be deposited on ceramic substrate (resistive sensor) or on FET structure as a gate. Such FET transistor with C-nPd film gate (FET/C-nPd) was elaborated and patented by us [1011].

The discussed sensors, under the influence of different hydrogen gas concentrations have different specific initial resistance. The initial resistance obtained samples are shown in Table 1.

To examine changes of resistance transistors with carbon-palladium thin films (FET/C-Pd) and resistive carbon-palladium (C-nPd film) films due to hydrogen gas presence we use special measure equipment that was built in Sieć Badawcza Łukasiewicz Instytut Tele- i Radiotechniczny. Schema of this measure equipment is shown in Figure 1. The measure equipment consists of gas cylinders, flow controllers, mixer of gas, valves, measure chamber, measuring system, power supply.

Tab.1. The initial resistance of samples

	R, kΩ
Sample 1	0,92
Sample 2	0,46
Sample 3	3
Sample 4	82,3
Sample 5	1
Sample 6	1

The measuring system controls the operation of the valves, performs measurements and accumulates results. The measuring system controls the operation of the valves, performs measurements and collects results in the files. The operator's task is to develop and implement measuring algorithms. In order to compare FET/C-nPd and C-nPd resistance changes due to hydrogen presence, we have developed a dedicated measuring algorithm. The heart of the developed measuring algorithm was to provide the hydrogen and nitrogen sequentially to measuring chamber in 10 minutes periods. It was a lot of time to achieve saturation sensors with hydrogen and rinsing them with nitrogen

We have measured resistance under influence 4% hydrogen in nitrogen for three samples of C-nPd (sample 1 to sample 3) and three samples of FET/C-nPd (sample 4 to sample 6).

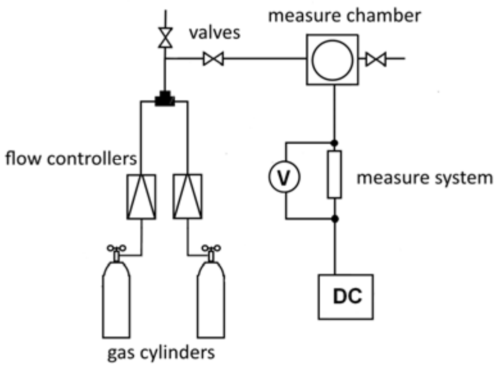
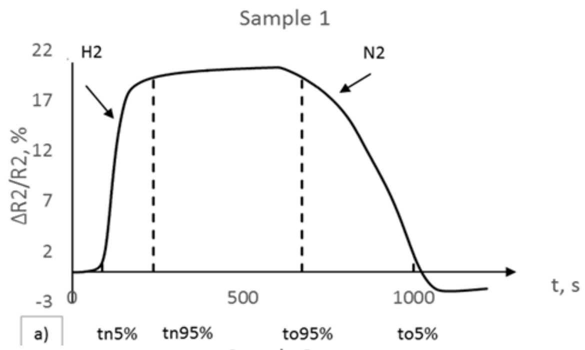


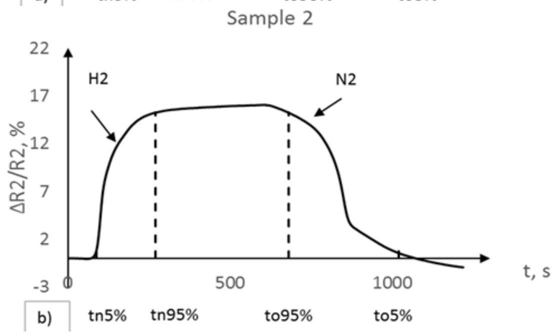
Fig.1 Measure equipment

Results and Discussion

We analyzed the registered results of measurements of resistance changes vs. hydrogen 4 H_2/N_2 % concentration for C-nPd samples and FET/C-nPd concentrating on the changes of of maximaml resistance and changes of time parameters such as: time when a value of measured resistance at 4% H_2/N_2 hydrogen concentration reaches 5 percent and 95 percent of maximal resistance value both for increasing and decreasing concertation of hydrogen in measured chamber.

The results of our measurements are shown in the Figure 2 and Figure 3 and in the Table 2.





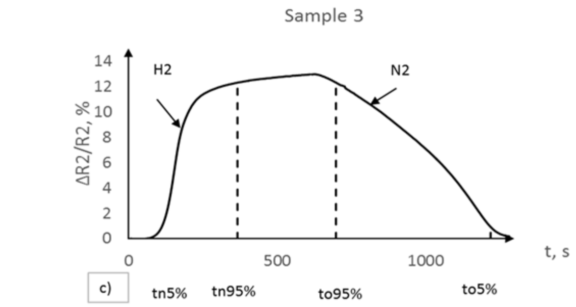


Fig.2 Changes of resistance: samples 1÷3 due to 4% H_2/N_2 concentration

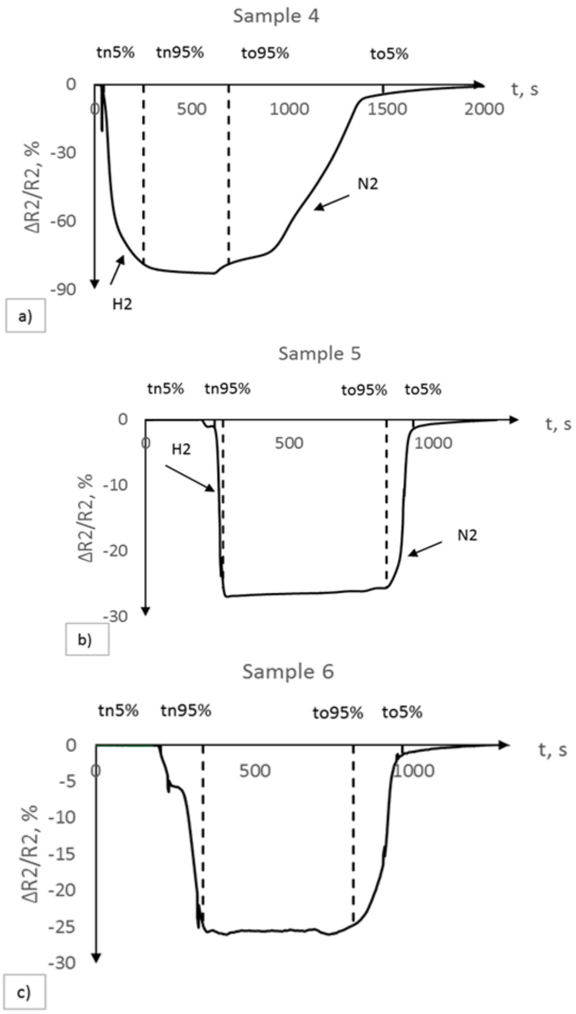


Fig.3 Changes of resistance Samples 4-6 due to 4% H_2/N_2 concentration

Tab. 2. The cumulative results of ΔR/R of all samples

	Sample 1	Sample 2	Sample 3	Sample 4	Sample5	Sample 6
ΔRmax, %	20,3	16,1	13,0	-82,9	-27,0	-26,1
tn95%	149,3	270,1	368,0	249,9	270,6	336,4
tn5%	88,7	87,6	104,8	44,3	241,1	204,3
to95%	673,7	679,4	698,3	689,9	837,3	809,4
to5%	1000,0	1020,0	1220,0	1481,4	932,7	965,1
Δtn , s	60,6	182,5	263,2	205,7	29,5	132,1
Δto, s	326,3	340,6	521,7	791,5	95,5	155,7

Legend: ΔRmax - max value of changes sensor resistance due to 4% H2/N2 presence, tn95% - point of time when when ΔR achieve 95% of ΔRmax for increasing concentration of hydrogen, tn5% - point of time when when ΔR achieve 5% of ΔRmax for increasing concentration of hydrogen, to95% - point of time when when ΔR achieve 95% of ΔRmax for falling concentration of hydrogen, to5% - point of time when when ΔR achieve 5% of ΔRmax for falling concentration of hydrogen, Δtn –difference betwin tn95% and tn5%, Δto –difference betwin to95% and to5%

The Figure 2 and Figure 3 show that for resistive sensors resistance increases when the measure chamber is gassed with H_2/N_2 while for all transistor samples the resistance decreases. This effect can be connected to formation of a channel area in the semiconductor between the source and drain due to the polarization of the gate by the presence of hydrogen. It is worth to notice that changes of maximal resistance reach during gassing the sensor are much higher for transistor samples than for resistive samples. The difference Δtn for both type of sensors are different and they depend on the analysis of ΔR/R plot show that the rise time (from t5 to t95) is much shorter for transistor sensors than for resistive sensor.

The highest changes of resistance has the sample 4. The highest rise time of response to H2 has sample 5. The lowest fall time of response have transistor samples sample 5 and sample 6. Although the sample4 has bigger value of rise and fall time than other samples, but it has many times higher response value.

Conclusions

The obtained measurement results show that transistor sensorshave better sensing properties than resistive sensors. FET/C-nPd sensors response (relative change in resistance ΔRmax/R under the influence of 4% of hydrogen) is higher than for resistive sensors

The FET/C-nPd transistor sensors with have better sensing properties than the resistive C-nPd sensors. Nevertheless, C-nPd sensors have a simpler structure and are cheaper to produce. The main advantage of both types of sensors is the lack of the need to heat the structure, which causes a much lower power consumption than the sensors currently used.

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