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HYDROGEN SENSOR BASED ON FIELD EFFECT TRANSISTOR WITH C-PD LAYER

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Abstract

ISFET (Ion Sensitive Field Effect Transistors) microsensors are widely used for pH measurements as well as analytical and biomedical applications. At the same time, ISFET is a good candidate for testing various materials for their applications in sensitive membranes. For example, hydrogen sensitive carbonaceous films containing Pd nanocrystallites (C–Pd) make this material very interesting for sensor applications. A cost effective silicon technology was selected to fabricate n-channel transistors. The structures were coupled to specially designed double-sided PCB (Printed Circuit Board) holder. The holder enables assembly of the structure as part of an automatic stand. The last step of production of MIS structures was deposition of the C–Pd layer. The C–Pd films were fabricated by the Physical Vapor Deposition (PVD) method in which C60 and palladium acetate were evaporated. Electrical resistance of structures with C–Pd films was measured during their interaction with hydrogen. Finally, a new type of highly sensitive FET hydrogen sensor with C–Pd layer was demonstrated and characterized.

Keywords: FET, C–Pd layer, hydrogen sensor, field effect transistor.

1. Introduction

ISFET (*Ion Sensitive Field Effect Transistors*) microsensors are widely used for pH measurements [1], analytical and biomedical applications [2] and monitoring of water pollution [3–5]. At the same time, ISFET is a good candidate for testing various materials for application in sensitive membranes [6]. A new dielectric (*e.g.* DLC (*diamond-like carbon*), AlN, Al_2O_3) [1, 7, 8] or 2D materials (*e.g.* graphene) [9] can be applied instead of commonly used stacked gate structure of Si_3N_4/SiO_2. We propose to apply a new nanocomposite of carbon-palladium (C–Pd) film for this purpose. Its properties such as high sensitivity to hydrogen make this material very interesting for sensor applications. Palladium-based H_2-sensing techniques can be categorized as electrical, optical, strain and chemi-mechanical methods depending on the physical parameters under detection. The electrical and strain-based methods can be used to measure changes in electrical

properties (resistance or conductance) or sample dimensions, respectively. Palladium-based optical sensors detect changes in optical properties (reflectance or transmittance). All these changes result from absorption of hydrogen atoms in the palladium volume. The optical method is faster and safer due to elimination of interference-sensitive electrical signals and is more convenient for remote detection in hazardous environments. The chemi-mechanical sensors detect changes in the mechanical properties of small sensing structures. The microcantilevers fabricated by *micro-electro-mechanical system* (MEMS) processes are a good example.

Palladium has been well-known as a hydrogen sensitive material since the 19th century. Hydrogen diffusion through heated palladium was demonstrated by Graham [10] Since then, many other researchers have conducted extensive studies of interaction of palladium and hydrogen. Recently, it has been found that palladium as a nanograin material (nano-palladium) enhances adsorption/desorption properties of hydrogen in comparison with Pd bulk material [11-14]. Our studies on carbon-palladium nanocomposites show that such a system is much more stable than nano-palladium and can be applied as a fast and sensitive hydrogen detector [15–17]. The results of our study reveal that such a nanocomposite can be made of a carbonaceous matrix, transparent for hydrogen and stabilizing Pd nanograins (fcc type, with sizes between 2 and 20 nm [15, 17] depending on the technological parameters) placed in this matrix. Low-dimensional Pd nanostructures have been found to exhibit resistance-increasing for H_2 adsorption as in the bulk Pd sensors. Hydrogen detection performance of the Pd nanostructures is generally better than for bulk Pd due to increased surface-to-volume ratio.

The idea of producing gas sensors based on transistor structures is widely known [18], and, in the case of palladium layers working as a gate metallization in a field effect transistor, the topic dates back to the mid-seventies [19]. Both field effect structures, such as capacitors and transistors have been reported in the literature. MOS (*Metal Oxide Semiconductor*) devices with Pt or Pd electrodes have been developed, implemented and are successfully used [20]. In [21] hydrogen sensor based on FET with platinum and iridium gate were examined. The current state of research and review of the use of palladium and palladium-based nanostructures for hydrogen detection [22] allows defining the manufactured devices as a new type of solution because hydrogen sensors based on field-effect transistors are usually implemented with a metallic palladium gate, sometimes as palladium grains on nanotubes which are transferred to the channel area of the transistor [23].

During the implementation of projects dedicated to the development of C–Pd nanocomposite technology, it was found that the deposition of such a film on the transistor structure of an open-gate [2] leads to creation of a very fast and sensitive hydrogen sensor.

The obtained FET devices should no longer be considered exclusively as ISFET structures, which are intended to measure chemical solutions and detecting ions, although their design is identical but it is used for measuring gases.

In this paper we present the technology for producing such a transistor and the sensor properties of the proposed structure.

2. Experimental details

2.1. FET structure technology

The technology of the FET hydrogen sensor is presented in Fig. 1. A cost effective silicon technology was selected to fabricate n-channel transistors. The first step in the process of producing FET structures is thermal oxidation to obtain a field oxide with a thickness of about 440 nm

Metrol. Meas. Syst., Vol. 27 (2020), No. 2, pp. 313–321
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(Fig. 1A). A p-type silicon, ⟨100⟩-oriented, with resistivity of 6–8 Ω·cm was used as a substrate. After the first photolithography windows were opened to drain and source areas for phosphorus (Fig. 1B). After the cleaning process, a 20 nm-thick layer of SiO_2 was fabricated through thermal oxidation (Fig. 1C). Another photolithography defined the areas of etching process. In the next step the contact windows for metallization were opened (Fig. 1D) and a layer of aluminum was evaporated (Fig. 1E). The structures were coupled to a specially designed double-sided PCB (*Printed Circuit Board*) holder and then electrically connected using 100 μm wire bonding with the ultracompression technique. The holder enables assembly of the structure as part of an automatic stand. The final step in the production of MIS structures is the deposition of C–Pd layer [15] (Fig. 1F).

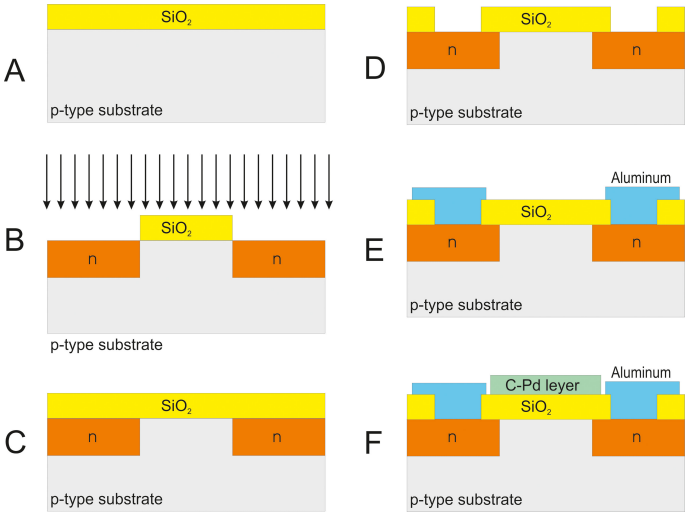

Fig. 1. Steps of the FET fabrication process with the cross section of the structures.

2.2. C–Pd layer technology

The C–Pd nanocomposite films were obtained through *Physical Vapor Deposition* (PVD) in which C60 and palladium acetate were evaporated from two separate sources under a dynamic vacuum of 10^{-6} mbar. The technological parameters such as deposition time, current through evaporation sources and distance between the substrate and the sources were important for the preparation of film with an adequate resistance and structure. The deposition method itself and properties of fabricated C–Pd layers were presented in our previous works [15–17]. The TEM (*Transmission Electron Microscope*) and SEM (*Scanning Electron Microscope*) images of such a nanocomposite film structure are shown in Fig. 2a and 2b, respectively. Figure 2b presents the gate area of the FET structures. The layer composition was shown in Fig. 2c.

2.3. Electrical measurements

Both the transfer and output characteristics were measured prior to the deposition of C–Pd layers to check the correctness of process flow and operation of the final transistors. The test used deionized water dropped into the gate area of the FET transistor. The drain-source and gate-source voltage ranges did not exceed 5 V.

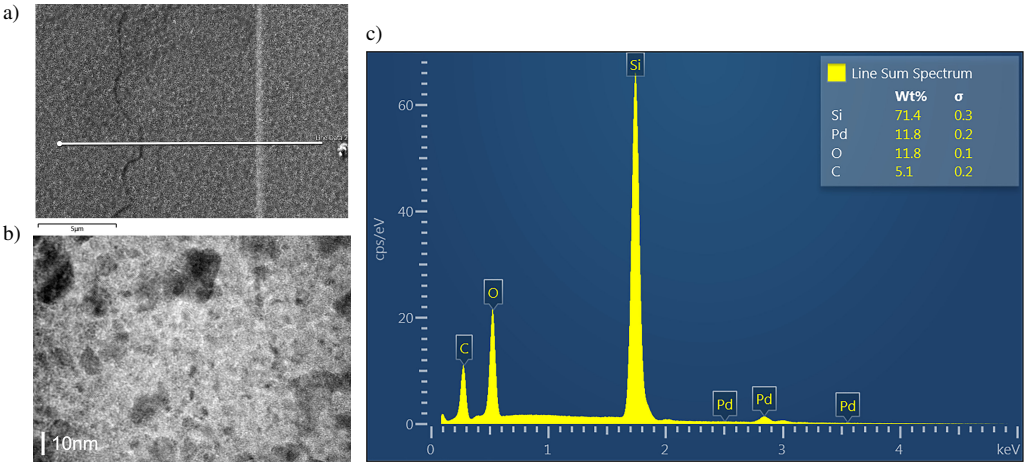

Fig. 2. TEM (a) and SEM (b) images and EDS (c) results of the investigated H_2-sensitive C–Pd layer.

The measurement of changes in sensor resistance occurring during a change in hydrogen concentration was carried out using a set-up whose block diagram is shown in Fig. 3.

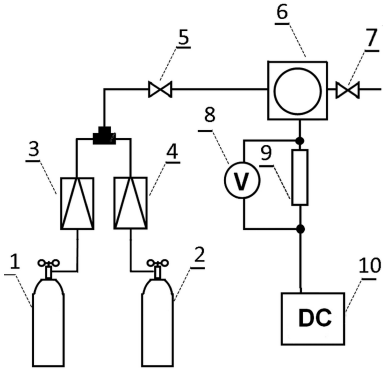

Fig. 3. Hydrogen measurement setup: 1, 2 – gas bottles, 3, 4 – mass flow controllers, 5 – gas mixer, 6, 8, 10 – valves, 7 – 50 ml measurement chamber, 9 – measuring system, 11 – voltage source.

The flow of H_2/N_2 mixture was set at the level of 50 ml/min. The measurements were carried out at room temperature and atmospheric pressure. This set-up allows measurements of changes in electrical resistance for a precisely determined H_2 concentration during the absorption/desorption cycles carried out by filling and evacuating the measuring chamber with hydrogen via a pump and valve system. Hydrogen desorption was obtained in an air flow.

A measurement chamber was used to determine the sensitivity of films to hydrogen. The set-up of the measuring chamber has an electric feedthrough, gas inlet and outlet. The gas inlet was driven by a mass flow controller. The electrical resistance of C–Pd films was measured during their interaction with hydrogen and air.

The transistor resistance measurements with C–Pd films were performed cyclically as follows. First, a mixture of hydrogen and nitrogen was passed through the measuring chamber for about 10

Metrol. Meas. Syst., Vol. 27 (2020), No. 2, pp. 313–321
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minutes (gas flow rate of 50 ml/min). To conduct the experiment two concentrations of hydrogen were used, the biggest for our set-up of 3.97% H_2/N_2 and the smallest one of 0.022% H_2/N_2. The resistance measurements were carried out continuously with changes recorded every 0.3 s.

3. Results

The transfer and output I–V characteristics of FET are presented in Fig. 4a and 4b, respectively. The characteristics obtained are reproducible and show correct operation of the test structures. The calculated threshold voltage was around 1 V and depends on the location of the measured structure on the silicon wafer. The results described above showed the correct operation of the

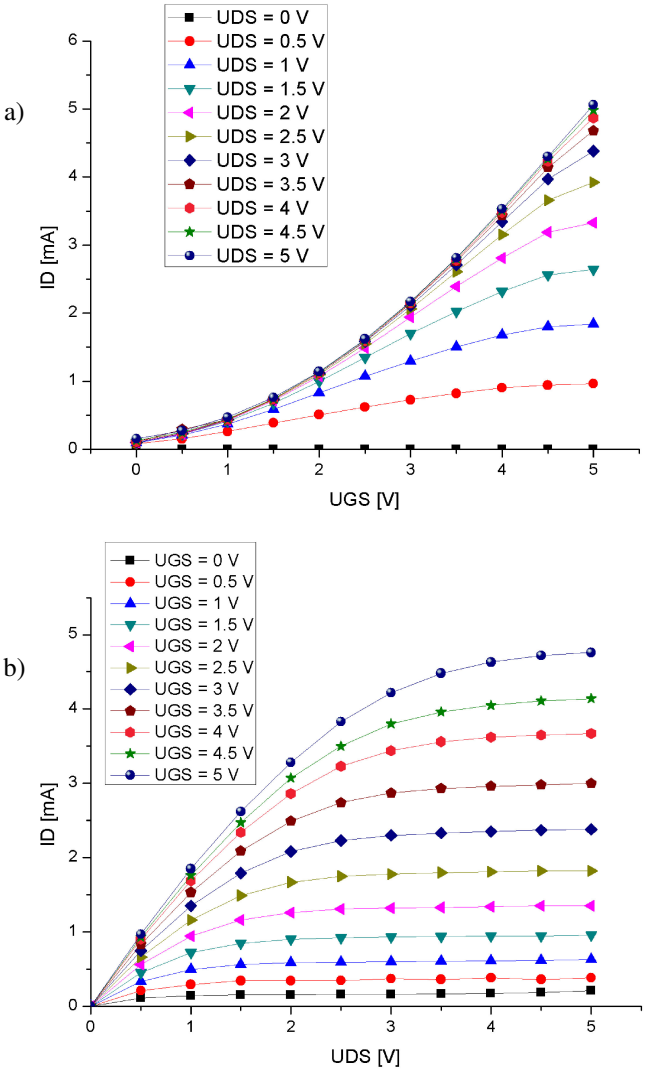

Fig. 4. The transfer (a) and output (b) I–V characteristics of the produced transistors.

assembled structures and enabled the implementation of the last stage of H_2 sensor realization – the deposition of a hydrogen-sensitive layer.

The influence of hydrogen on channel resistivity of sensors produced on the basis of the field effect transistor is presented in Fig. 5, Fig. 6. and Fig. 7.

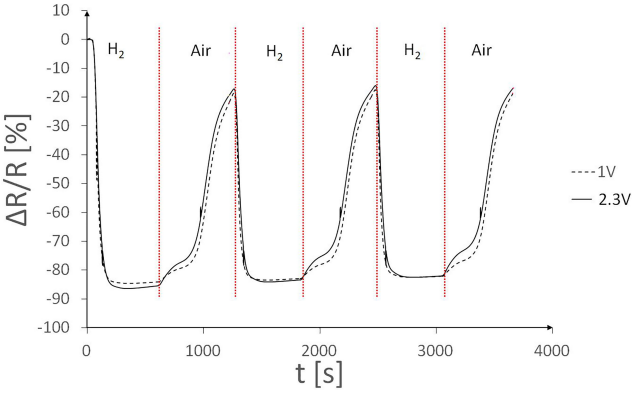

Fig. 5. Relative changes in C–Pd transistor resistance under 3.97% hydrogen concentration.

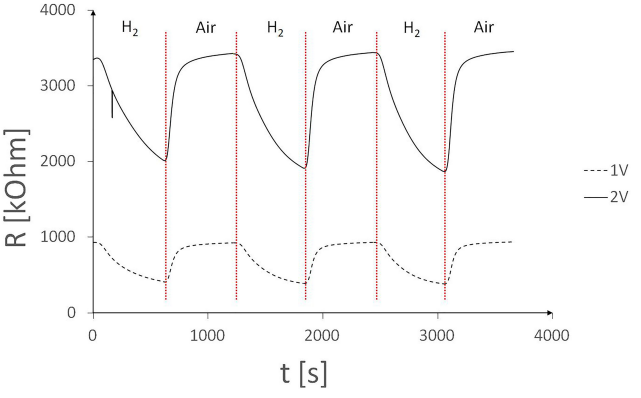

Fig. 6. Absolute changes in C–Pd transistor resistance under 3.97% hydrogen concentration.

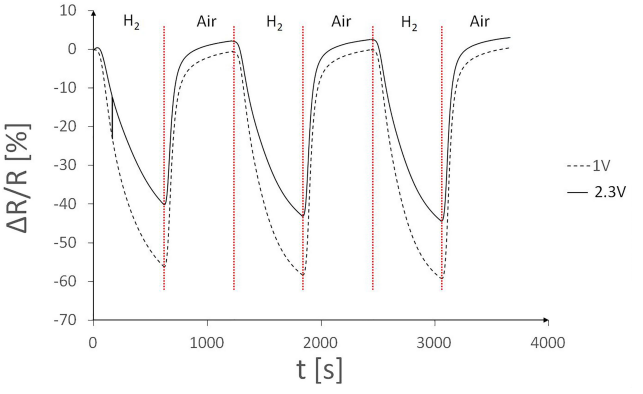

Fig. 7. Relative changes in C–Pd transistor resistance under 0.022% hydrogen concentration.

Such a strong reaction to the presence of hydrogen results from the use of the C–Pd layer as transistor material in the transistor's gate area.

The physical basis of hydrogen detection is very similar to classic structures of FET sensors with palladium metal gates. The hydrogen molecules reaching palladium (in this case, palladium nanoparticles) dissociate. The dissociative adsorption of H_2 on the Pd grain surface followed by diffusion through the carbon layer form dipoles at the C–Pd/SiO_2 interface. This changes the flat-band voltage and, as a result, the threshold voltage of the transistor [24, 25].

The changes in the charge of the H_2-sensitive layer translate into channel area modification which causes the drain current to change following a change in channel resistance. As the transistor structures operate based on the influence of electric field, a small change of charge in the gate area is clearly visible in the current-voltage characteristics and parameters of these devices. The presented sensor with a relative change in resistance of up to 90% is much more sensitive than previously implemented structures based on the change of resistance of the C–Pd layer itself under the influence of hydrogen, where the change did not exceed 12% [26].

The relatively long response time is associated with the design of the measuring chamber and the gas flow rate. The measuring chamber with piping has a capacity of about 150 ml. Full nominal concentration is achieved with a gas flow of 50 ml/min after 3 minutes. If this time is taken into account when introducing hydrogen, it can be seen that the layer reacts appropriately to changes in concentration. Still worse, when the sensor returns to its original state before detection, the process is indeed relatively slow. The simplest, intuitive solution is to heat a small, detection mass of the sensor which will definitely increase the desorption efficiency.

At high hydrogen concentrations, the effect of U_{DS} voltage on sensing properties is visible but does not appear to be significant. However, when the detected hydrogen concentration is at the level of 200-ppm the difference in the structure reaction is very pronounced. The analysis of this impact will be the subject of our further research, which will also consider the effect of substrate polarization on the results obtained.

Measurements have shown that it is possible to identify hydrogen concentrations even below the 220-ppm level. The relative change in transistor channel resistance for such hydrogen concentration is still at a level when it is not difficult to detect.

4. Conclusions

A new type of a highly sensitive FET hydrogen sensor with a C–Pd layer was prepared and characterized. The presented sensor design uses a nanocomposite C–Pd layer produced on the SiO_2 layer as the gate of a field-effect transistor. Typically, the design of FET hydrogen sensors is based on the use of a catalytic metal in the gate area. In this case, the advantages of using nanoparticles and FET structures have been combined. On the one hand, this resulted in creation of high-sensitivity devices that can affect the detection properties by changing the parameters of the C–Pd deposition process and, in addition, the use of nanomaterials in place of metallic palladium causes a significant reduction in the production costs of the hydrogen sensor.

The obtained results show that in some cases the relative change in channel resistance due to the presence of hydrogen exceeds 80%. A detection of hydrogen at the level of 220-ppm is still attainable. The measurement results indicate that the value of the supply voltage also has an impact on the level of resistance change.

The relatively long response times are associated with the design of the measuring chamber and the gas flow rate and desorption process. The simplest, intuitive solution is to heat a small, detection mass of the sensor. On the other hand, the response of gas sensors is not always the

critical parameter because in real conditions gas exchange usually does not occur quickly, so the importance of the gas sensor response time depends on its specific application.

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