ХІМІЧНІ СЕНСОРИ

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H_2O_2 SENSOR BASED ON MOSFET WITH ACTIVE LAYER IN SUBSTRATE AREA

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H_2O_2 SENSOR BASED ON MOSFET WITH ACTIVE BACK-GATE PART OF SUBSTRATE

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Abstract. Sensors based on MOSFET with por-Si layer at the back-gate part and with H2O2 catalyst (Pt-nanoparticles) investigation was done. Back-gate changes were done by MASE technology. The porous structure analysis, measurement dimension of Pt nanoparticles was performed. And also we represented the influence thus nanoparticles for sensor sensitivity. Using approximation output curves

at different concentration H_2O_2, we calculated sensitivity of our sensor and it's reach at least 0,135 μA/ppm. The energetic activity of the catalytic reaction H2O2 was calculated. And also we calculated the influence of this effect on the experimental results.

Keywords: MOSFET, sensor, hydrogen peroxide, porous Si, Pt-nanoparticles

СЕНСОР ПЕРЕКИСУ ВОДНЮ НА ОСНОВІ МДН-ТРАНЗИСТОРА З АКТИВНИМ ШАРОМ В ОБЛАСТІ ПІДКЛАДКИ

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Анотація. Проведено дослідження сенсорів H_2O_2 на основі МДН-транзисторів з шаром пористого кремнію та каталізатором перекису водню (наночастинками платини) на зворотній стороні підкладки в області затвору. Модифікація тильної сторони сенсора виконувалася шляхом метал-стимульованого хімічного травлення. Проведено аналіз пористої структури, вимірювання розміру наночастинок платини та їх вплив на чутливість сенсора. На основі апроксимації вольт-амперних характеристик при різних концентраціях перекису водню обчислено чутливість сенсора, що складає не менше 0,135 мкА/ppm. Розраховано енергетичну активність реакції каталітичного розпаду H_2O_2 та її вплив на результати експерименту.

Ключові слова: МДН-транзистор, сенсор, перекис водню, пористий кремній, Pt наночастинки

СЕНСОР ПЕРЕКИСИ ВОДОРОДА НА БАЗЕ МОП-ТРАНЗИСТОРА С АКТИВНЫМ СЛОЕМ В ОБЛАСТИ ПОДЛОЖДКИ

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Аннотация. Было проведено исследования сенсоров на базе МДН-транзисторов со слоем пористого кремния и катализатором перекиси водорода (наночастицами платины) на обратной стороне подложки со стороны затвора. Изменения тыльной стороны сенсора производилась методом металл-стимулированного химического травления. Произведено анализ пористой структуры, измерено размер наночастиц платины и их влияние на чувствительность сенсора. Используя аппроксимации вольт-амперных характеристик при разных концентрациях перекиси водорода рассчитано чувствительность сенсора, которая составляет не менее 0,135 мкА/ppm. Рассчитано энергетическую активность реакции каталитического распада H_2O_2 та ее влияние на результаты эксперимента.

Ключевые слова: МДН-транзистор, сенсор, перекис водорода, пористый кремний, Pt наночастицы

Introduction

The application of hydrogen peroxide (H_2O_2) in many technological processes, in particular in medicine and agriculture, is based on its oxidizing properties. The process of H_2O_2 dissociation in aqueous solutions occurs freely. A rate of the dissociation can be accelerated using liquid catalysts, both anions and cations, as well as solids (coal, metals, salts and metal oxides). Also, the process of catalytic H_2O_2 dissociation is effected by the pH of the media as well as by the state the active surface. In cells of plants, animals and humans body the catalytic H_2O_2 dissociation occurs under influence of catalase and peroxidase enzymes, which, unlike catalysts of nonbiological origin, have extrimly high catalytic activity and specificity.

The detection and control of H_2O_2 concentration are very important for pharmacy, medicine, industry. Moreover, H_2O_2 is used for bleaching, for the treatment of wastewater, in the petrochemical, woodworking and paper industries, thus playing an important role in the modern industrial world. Nowadays hydrogen peroxide sensors are also widely used as a chemical sensor, since hydrogen peroxide is a product of many biological reactions, including the peroxidase and catalase mediated dissociation [1]. The level of hydrogen peroxide in food products makes it possible to assess the degree of pollution with pesticides, which in turn allows to determine the quality of these products. Another field of H_2O_2 sensors application H_2O_2 is an immuno-enzymatic analysis based on peroxidase.

Basic modern methods determining the concentration of hydrogen peroxide are based on chemical reactions or refractometry, which require special knowledge and equipment. However, there is a need in such sensors for household and outdoor condition, which are required to be cheap, simple in use and reliable. Usually for such purposes electrochemical reactions based on the interaction of hydrogen peroxide with metals [1-4] are used. Therefore, the development of a high-sensitive hydrogen peroxide sensors is still a challenging problem.

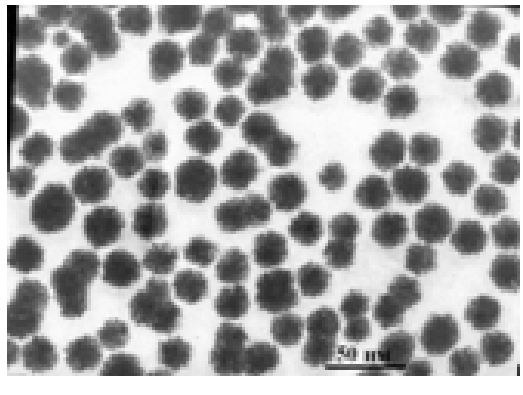
In our study a combination of a porous silicon structure and deposition of platinum nanoparticles was proposed. Such combination enhances a sensitivity of the sensor due to a significant increase of surface area of the porous layer.

Methods

The developed sensor is based on metal-insulator-semiconductor (MIS) field-effect transistor with p-type channel. Field-effect transistor, was produced on silicon wafers doped with phosphorous (n-type), resistance 4.5 Ω/□ ,with (100) orientation and thickness of 450 μm were used. SiO_2-CeO_2 system was used as gate dielectric with thicknesses of SiO_2 and CeO_2 layers of 10 nm and 50 nm, correspondingly were used as a gate dielectric. Silicon oxide was grown on a substrate by thermal oxidation of the silicon, then a thin cerium oxide film was deposited on the surface by the method of "metallic mirror» oxidation. Aluminum was used as an ohmic contact to p-Si.

Pt nanoparticles were obtained by chemical reduction of $PtCl_6^{2-}$and ascorbic acid ions. In a mixture of aqueous solutions $H_2PtCl_6 \cdot 6H_2O$ (CPt = 200 mg / dm^3) and $C_6H_8O_6$ ($5 \cdot 10^{-2}$ mol/dm^3) quasipheric particles with an average size of 26 nm were formed for 24 hours at 40°C. [5].

A porous silicon structure formed on the back side of the field-effect transistor with deposited on it catalyst, Pt nanoparticles, simultaneously serves as an working and sensitive area of the sensor. Such structure was formed in two stages: first, a dosed drop of a solution of nanoparticles was applied on a silicon surface. Then the metal-stimulated chemical etching of silicon was performed in a solution of 5M NF + 0,3M H_2O_2 at room temperature for 90 minutes. As a result of this process, the etching of silicon under the nanoparticles Pt occurs in the (100) direction [6,7]. Images of the Pt nanoparticles on the back side of the sensor (Fig. 1) were obtained with electron microscope JEM 2000FXII, the scanning electron microscope JEOL, JEM 2100 HR and the Atomic-force microscope (SOLVER Nano), respectively.



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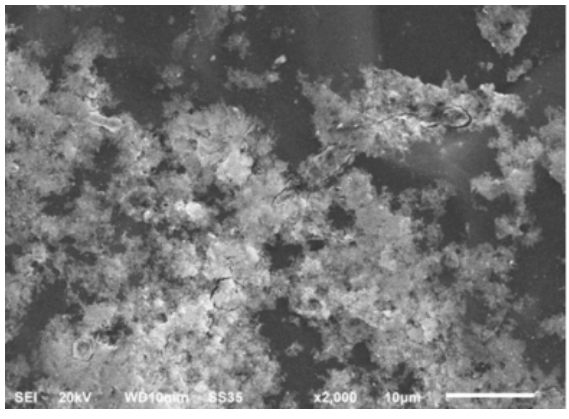

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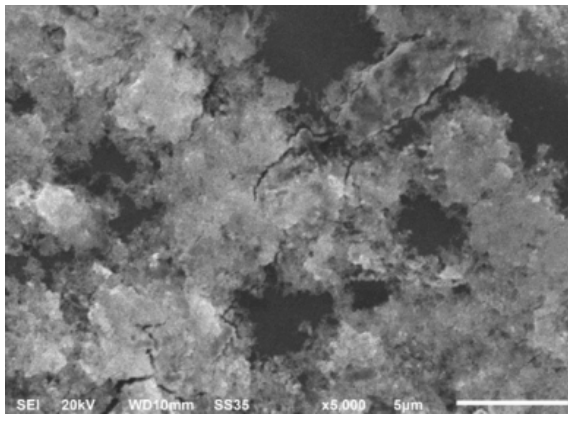

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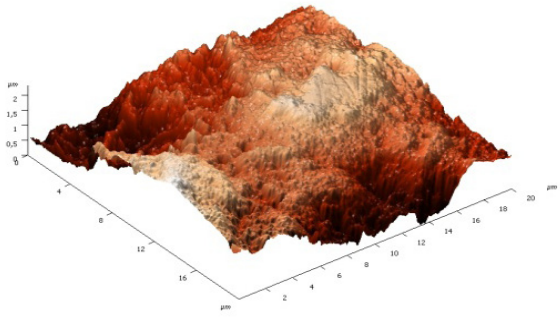
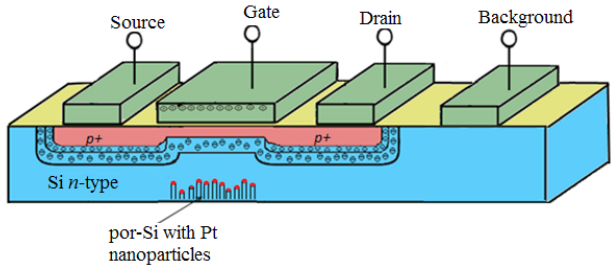


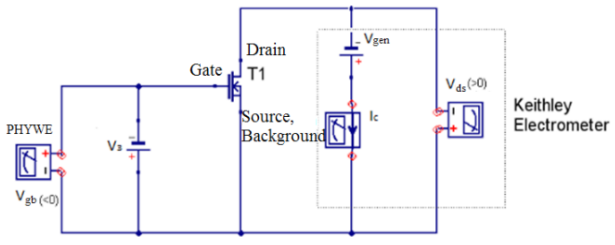
(d)

Fig.1 SEM images of platinum nanoparticles on the back side of the field-effect transistor (a) with resolution of 2000 (b), 5000 (c) and a three-dimensional image of the sensor's functional area the with porous silicon and Pt nanoparticles (d).

The sensor's functional area containing a layer of porous silicon and immobilized in it Pt nanoparticles is shown on Fig. 2.



(a)



(b)

Fig. 2 Sensor structure (a) and measurement electrical circuit (b).

Electrical circuit for the main measurements of the sensor at different concentrations of hydrogen peroxide is shown on Fig 2.

The experiment was carried out at room temperature (18°C) in the concentration range of 25-100 ppm. Solutions of hydrogen peroxide were prepared by diluting H_2O_2 60%, produced by Grupa Azoty Zakłady Azotowe «Puławy» S.A. The reverse bias of voltage equal to 11.5 V was selected from the drain-gate characteristics of the transistor (Fig. 3). The operating drain-source voltage was in range of 3-4 V.

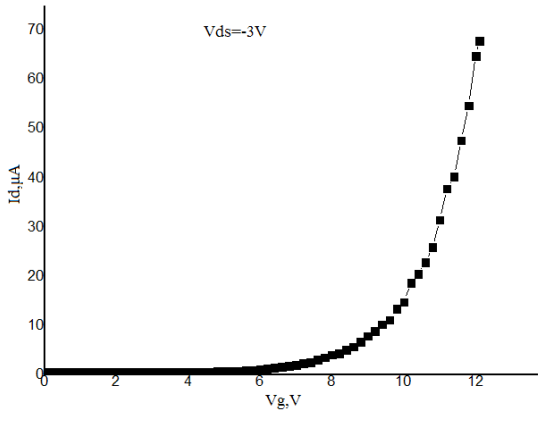


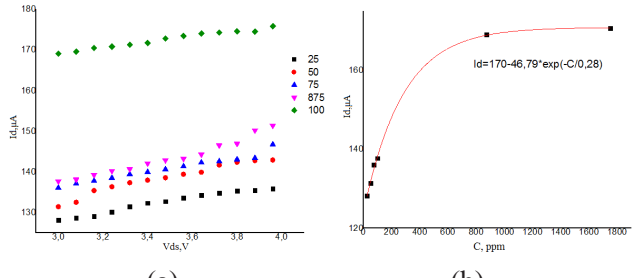
Fig. 3. A drain-gate characteristic of the transistor with Pt nanoparticles.

Results and Discussion

During the reaction of catalytic H_2O_2 dissociation an exchange of electrons between the catalyst and hydrogen peroxide occurs in solution, which leads to extraction of charge carriers from the substrate and, consequently, to changes in the conductance of the channel. Offset of the threshold voltage or change of the drain current can serve as an indication of reaction of the sensor to change the hydrogen peroxide concentration. With an increase in the H_2O_2 concentration the level of positive charges on the sensor surface rises as a result of H_2O_2 dissociation. Since a p-channel MOS transistor is used, an increase in the positive charge on the its active surface leads to the extraction of electrons from the substrate, which increases the channel conductance which, in turn, leads to increase drain current.

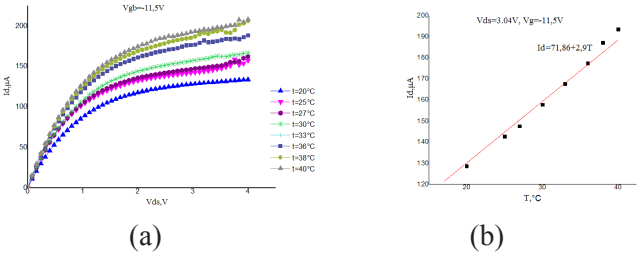
The sensor's response to various concentrations of hydrogen peroxide was studied using I-V curves in the drain- source voltage range of 3-4V (Fig. 4a).

The dependence of the drain current on the concentration of hydrogen peroxide is approximated by a reverse exponential function (Fig. 4b), apparently due to the saturation of the sensitive region with products of the reaction at high concentrations. This problem can be overcomed by increasing the gate size and sensitive area of the sensor.



(a) (b)

Fig.4. Output characteristics of the transistor at hydrogen peroxide concentrations of 25-100 ppm (a) and the dependence of the drain current on the concentration H_2O_2 at V_{ds} = 3.04V (b).



(a) (b)

Fig.5. Temperature dependence of the sensor: I-V characteristics at different temperatures (a); and temperature dependence of drain current at V_{ds}=3,04V (b).

In addition to measuring the I-V characteristics, a study of the temperature dependence of the drain current was performed, which demonstrated the linear dependence of resistance on temperature (Fig. 5). The temperature coefficient was about 2.9 μA/°C. To take into account the influence of temperature during measurement of low H_2O_2 concentrations it is reasonable to incorporate a temperature sensor to our sensor. As a result of the dissociation of 1.2 g hydrogen peroxide, only 0.3 mJ of heat is emitted, and for heating of a plate to 1 °C 0.2 J of energy is required. The obtained calculations of the energetic activity of hydrogen peroxide indicate that the reaction of catalytic dissociation of such volume of H_2O_2 does not affect the temperature change of the sensor structure itself, and, thus, does not influence the results of sensor operation.

Also, to increase the sensitivity of the structure the substrate thickness should be reduced before formation of the porous silicon layer.

Conclusions

In this study a prototype of the transistor based on MOS transistor was proposed and produced. This prototype is controlled not through a reference electrode as in standard model, but through the change of the electrical potential of a modified back side of a substrate as a result of the electrochemical reaction on the surface of the porous silicon with platinum nanoparticles. The sensitivity of the proposed sensors is at least of 0.135 μA/ppm, and the temperature coefficient is of 2.9 μA/°C. Such characteristics create the possibility to use this sensor not only for the direct determination of hydrogen peroxide concentration, but also expands the range of its applications, for example, for the detection of other biochemical substances of interest.

References

[1]. Chen, S., Yuan, R., Chai, Y. et al. Electrochemical sensing of hydrogen peroxide using metal nanoparticles: a review Microchim Acta (2013) 180: 15.

[2]. Ren, C., Song, Y., Li, Z. et al. Hydrogen peroxide sensor based on horseradish peroxidase immobilized on a silver nanoparticles/cysteamine/gold electrode Anal Bioanal Chem (2005) 381: 1179.

[3]. Wang, Q. & Zheng, J. Electrodeposition

of silver nanoparticles on a zinc oxide film: improvement of amperometric sensing sensitivity and stability for hydrogen peroxide determination Microchim Acta (2010) 169: 361.

[4]. Wang, L., Zhu, H., Hou, H. et al. A novel hydrogen peroxide sensor based on Ag nanoparticles electrodeposited on chitosan-graphene oxide/cysteamine-modified gold electrode J Solid State Electrochem (2012) 16: 1693.

[5]. Estrela-Lopis V.R., Borodinova T.I., Yurkova I.N., Extracellular biomeneralization and synthesis of nano- and microcrystals of gold and platinum in aqueous solutions of polysaccharides. In the book: "Colloid-chemical bases of nanoscience" / Ed. A.P. Shpaka, Z.R. Ulberg. - K.: Academperiodica, 2005. – 238-297.

[6]. Zhipeng Huang, Xuanxiong Zhang, Manfred Reiche, Lifeng Liu, Woo Lee, Tomohiro Shimizu, Stephan Senz, and Ulrich Gösele, Extended arrays of vertically aligned sub-10 nm diameter [100] Si nanowires by metal-assisted chemical etching, Nano Letters – 2008, Vol. 8, No. 9, 3045-3051.

[7]. Zhipeng Huang, Nadine Geyer, Peter Werner, Johannes de Boor, Ulrich Gösele, Metal-Assisted Chemical Etching of silicon: A Review, Adv. Mater - 2011, 23, 285–308.

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Summary

Determination and control of hydrogen peroxide concentration are very important in pharmacy, medicine, and other industries. So there is a need of simple, low-cost and reliable sensors for field and everyday use.

In the paper sensor based on the p-channel field-effect transistor of metal-insulator-semiconductor type improved with a combination of porous silicon structure with platinum nanoparticles is proposed.

Porous silicon active structure was formed on the rear side of FET. The structure was formed in two steps: first, a dosed drop of Pt nanoparticles solution was applied on a silicon surface by spin coating and after this metal-assisted chemical etching was performed.

Unlike conventional FET sensors control is providing not by comparison electrode but by changes of a potential of a modified rear side of the substrate via reaction on a porous silicon surface. During catalytic decomposition of hydrogen peroxide electrons exchange occurs in solution between catalyst and hydrogen peroxide. Increasing peroxide concentration leads to increase of positive charges quantity on working area surface. As p-channel MIS FET is used, the positive charge in the working area increase electron extraction from the substrate and consequently increase channel conductivity and drain current. The sensitivity of proposed sensors is up to 0,135 μA/ppm, and temperature coefficient is 2,9 μA/°C.

Such results allow using this sensor not only for direct hydrogen peroxide detection but also for detection of biological substances.

Keywords: FET, sensor, hydrogen peroxide, porous silicon, Pt nanoparticles

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Реферат

Визначення та контроль концентрації пероксиду водню на сьогодні є важливими в фармакології, медицині та інших галузях. Тому необхідні прості, недорогі та надійні сенсори для загальних лабораторних досліджень та повсякденного використання.

В статті запропоновано звичайна структура сенсору на основі р-канального польового транзистора типу металл-діелектрик-напівпровідник, але модифікований шляхом комбінації пористої структури кремнію з наночастинками платини.

Активна область з пористим кремнієм була сформована на зворотній стороні МДН-транзистора. Ця процедура відбувалася в два етапи: спочатку, дозована крапля розчину наночастинок Pt наносилась на поверхню кремнію, а на нступному кроці проводили метал стимульоване хімічне травлення.

На відміну від звичайних сенсорів на основі МДН-транзисторів, відгук сенсору реєструвався не з використанням електрода порівняння, а шляхом реєстрації зміни потенціалу модифікованої тильної сторони підкладки, як результат реакції впливу пористої поверхні кремнію з наночастинками Pt. Під час каталітичного розкладу перекису водню відбувається обмін електронами в розчині між каталізатором і перекисом водню.

Збільшення концентрації перекису призводить до збільшення кількості позитивних зарядів в робочій області. Оскільки використовувався р-канальний МДН-транзистор, то позитивний заряд у робочій зоні збільшує екстракцію електронів з підкладки і, як наслідок, підвищує провідність каналу та струм стоку. Чутливість запропонованих датчиків дорівнює 0,135 мкА/ppm, а температурний коефіцієнт складає всього лише 2,9 мкА/°С. Такі результати запропонованого сенсора дозволяють використовувати його не лише для виявлення H_2O_2, але також для виявлення біологічних речовин.

Ключові слова: МДН-транзистор, H_2O_2, пористий кремній, Pt наночастки