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Hydrogen Peroxide Measurements by MISFET and LET Structures with Rear Porous Silicon Layer and Metallic Nanoparticles

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***Abstract*—In the paper hydrogen peroxide MISFET and LET sensor performance is investigated. As hydrogen peroxide is a product of many chemical reactions, especially biological reactions, peroxide sensors are now widely used for detection of another. In this work, a combination of two nanostructures that are now used for hydrogen peroxide detection – porous silicon and metal nanoparticles was used.**

A MISFET (metal-insulator-semiconductor field effect transistor) was chosen as the basic sensor but unlike conventional FET sensors sensitive area was formed on the rear side of the sensor. In the aim to simplify sensor structure a LET (light-effect transistor) with sensitive area on the rear side was also tested. LET structure was produced by the same technology as FET, but then subgate system was removed by chemical etching. Porous silicon was formed by metal-assisted chemical etching (MACE) that consists of two stages. During the first stage, metallic nanoparticles are deposited on the surface by chemical or physical deposition. During second one these particles become catalysts of chemical reaction and pores are formed under them. Pore shape and density depend on both stages conditions.

Formation of porous silicon on the rear side leads to changes of substrate charge and influence gate-source curve as well as drain-source curve. Drain current for FET with an active area is lower due to the negative charge accumulated in porous silicon thanks to high tie connections concentration. Dependence of LET drain current on LED intensity (current) is almost linear and drain-source curves are similar to FET structure ones. FET samples with porous silicon/Pt and LET samples with porous silicon/Ag both show more stable and well-defined dependence of drain current on hydrogen peroxide concentration then samples without porous layer. All sensors have saturation of drain current from concentrations of hydrogen peroxide about 0.5-1% and dependence on concentration is first order exponential decay, obviously due to saturation of working area by reaction products or heating effect of hydrogen peroxide decomposition. In concentration range up to 0.3%

hydrogen peroxide best sensitivity was demonstrated by LET sensor (574 μA/%), for FET sensor sensitivity is about 6 μA/% for MISFET without active area and about 8.3 μA/% for MISFET with active area. As Ag and Pt catalyst hydrogen peroxide decomposition, sensors with metal nanoparticles shows quicker reaction (maximum response less than in 3 minutes). To ensure accuracy and precision of measurements temperature and illumination of active area dependences of drain current should be taken into account. MISFET with porous silicon demonstrates typical for silicon structures exponential decay dependence of drain current on luminous flux and quasi-linear dependence on temperature Slopes are 34 μA/lm and 6.46 μA/°C respectively.

Hydrogen peroxide sensor with porous silicon shows good performance in both configuration – as MISFET and as LET structure. MISFET structure is more adjustable but have lower sensitivity (about 8 μA/%) while LET structure is more simple and sensitive (up to 500 μA/%). Use of both Ag and Pt nanoparticles decrease response time of sensor to 2-3 minutes.

Ref 21, fig 17

Keywords— porous silicon; MISFET sensor; Pt nanoparticles, LET sensor, Ag nanoparticles

I. INTRODUCTION

H_2O_2 is a product of many chemical reactions, especially biological reactions, so peroxide sensors are now widely used for detection of another chemical [1] and the need of cheap and reliable sensors remains high.

Nanoparticles of noble metals are used in sensor applications [1]-[5] as active structure as well as a catalyst. Most common metals used for this purpose are Pt, Ag, and Au. Metal choice is determined by the substance to be identified and by sensor type [2].

As we concentrated on hydrogen peroxide detection and Ag and Pt were chosen because of its catalyst properties and inactivity against Si substrate.

On the other hand use of porous silicon increase active area surface and porous layer by itself can be used as detection structure of the sensor [6]-[12].

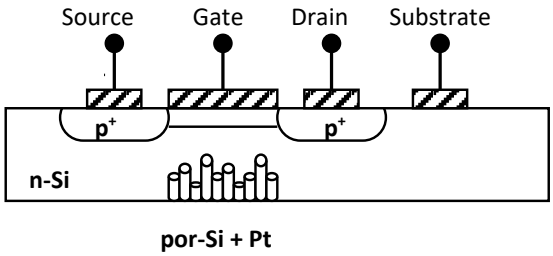

Fig. 1. FET sensor structure [17]

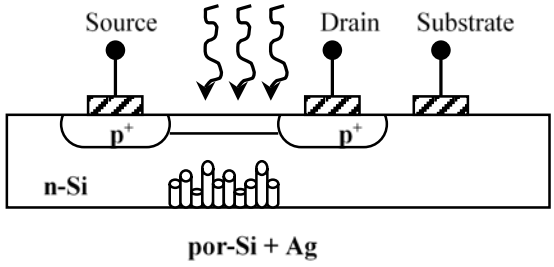

Fig. 2. LET sensor structure

In this work, a combination of two nanostructures – porous silicon and metal nanoparticles was used in the aim to determine best combination and technological process for hydrogen peroxide sensor formation.

There is two main types of hydrogen peroxide sensors – electrochemical sensors [13]-[15] and FET-based sensors [16],[17]. First type of sensors needs to be immersed in solution that is not always possible but the second type needs for detection only a very little amount of solution (less than 0.1 ml) that is more useful for in-field detection.

In this work a MISFET (metal-insulator-semiconductor field effect transistor) was chosen as the basic sensor but, unlike conventional FET sensors, sensitive area was formed on the rear side of the sensor [17].

In the aim to simplify sensor structure a LET (light-effect transistor) with sensitive area on the rear side was also tested.

II. SAMPLE PREPARATION

A. FET and LET structure

The sensor is based on the p-channel field-effect transistor of metal-insulator-semiconductor (MIS) type (fig 1). FET was produced on silicon wafers doped with phosphorous (n-type), resistance 4.5 Ω/m^2, orientation (111), thickness 450 μm. As subgate insulator system SiO_2 - CeO_2 (d_{SiO2} = 10 nm, d_{CeO2}=50 nm) was used. Silicon dioxide was produced by thermal oxidation and a thin film of cerium oxide was deposited by "oxidation of metallic mirror" method. Ohmic contacts to p-Si were made with Al

LET structure (fig.2) was produced by the same technology as FET above, but then subgate system was removed by chemical etching.

B. Nanoparticles formation and deposition

Platinum nanoparticles were produced by chemical reduction of $PtCl_6^{2-}$ ions by ascorbic acid. In a mixture of water solutions $H_2PtCl_6 \cdot 6H_2O$ (C_{Pt}=200 mg/dm^3) and $C_6H_8O_6$ ($5 \cdot 10^{-2}$ moles/dm^3) during 24 hours at 40°C quasispherical particles with average diameter of 26 nm are formed [15] Particles dimensions and sharp are almost regular as can be seen on SEM image of colloid (fig. 3). After spin coating deposition on the silicon surface Pt nanoparticles cover surface almost regulary and form linear-like conglomerates of few μm long (fig. 4)

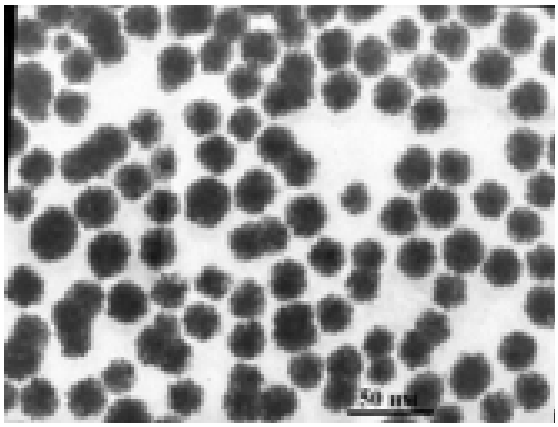

Fig. 3. SEM (JEM 2000FXII) image of Pt nanoparticles

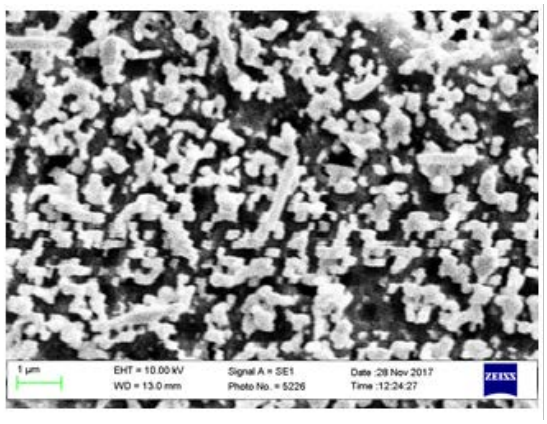

Fig. 4. SEM image of active area surface with Pt nanoparticles

Argentum nanoparticles were formed directly on the silicon surface from HF+$AgNO_3$ solution. Reaction time varied from 3 to 10 seconds.

Ag nanoparticles sharp and distribution are irregular; dimensions vary from few μm to hundred nm (fig. 5)

C. Metal-assisted chemical etching

Metal-assisted chemical etching (MACE) consists of two stages. During the first stage, metallic nanoparticles are deposited on the surface by chemical or physical deposition. During second one these particles become catalysts of chemical reaction and pores are formed under them. Pore shape and density depend on both stages conditions [18]. MACE process generally is more controlled than conventional porous silicon formation.

Porous silicon active structure was formed on the rear side of transistor.

First, nanoparticles were applied on silicon surface by spin coating (Pt) or chemical deposition (Ag) and after this metal-assisted chemical etching in 5M HF + 0,3M H2O2 solution was performed at room temperatures. In this way, etching occurs under nanoparticles in (100) direction. [19, 20] (fig. 6)

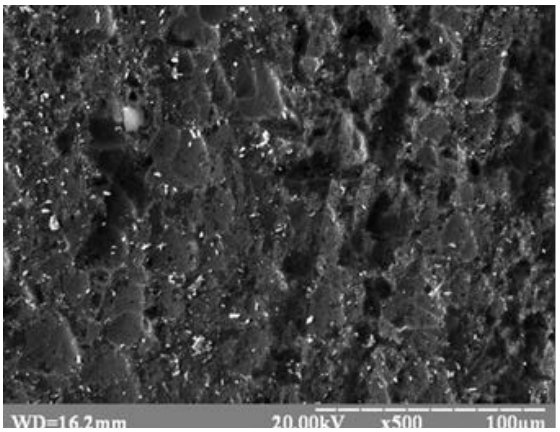

Fig. 5. SEM image of active area surface with Ag nanoparticles

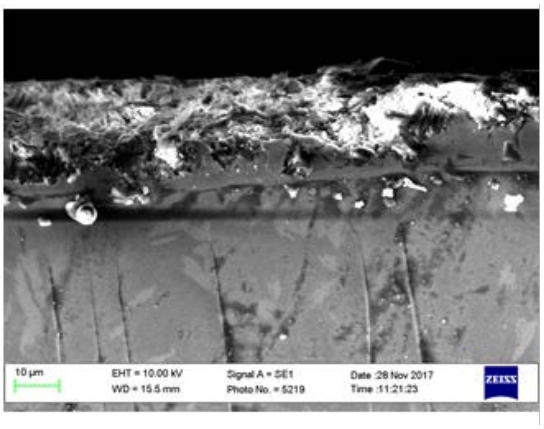

Fig. 6. SEM image of active area cross section

III. Results and Discussion

A. I-V curves

In the work, two FET structures were compared: a MISFET with porous silicon and Pt particles and a MISFET without active area.

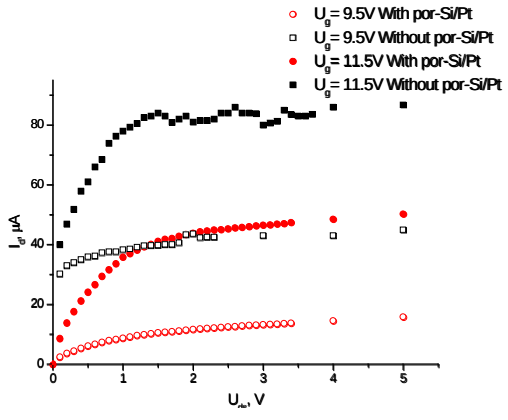

Fig. 7. Source-drain curves

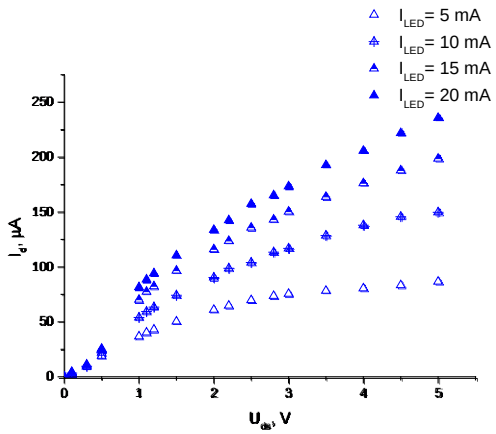

Fig. 8. Source-drain curves of LET at different LED intensity (current)

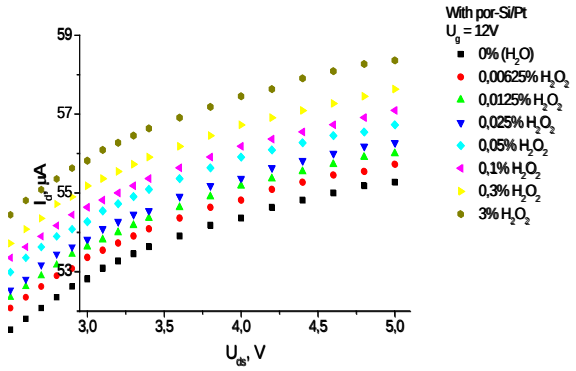

Fig. 9. Source-drain curves of MISFET with active area for different concentrations of H_2O_2

Formation of porous silicon on the rear side leads to changes of substrate charge and influence gate-source curve as well as drain-source curve (fig. 7). Drain current for FET with an active area is lower due to the negative charge accumulated in porous silicon thanks to high tie connections concentration.

Unlike FET structure LET structure drain current is controlled by light intensity. In this work a blue LED with intensity 6000-8000 mcd and wavelength 450 nm was used for gate control. Dependence of LET drain current on LED intensity (current) is almost linear and drain-source curves are similar to FET structure ones (fig. 8)

B. Concentration dependences

FET samples with porous silicon/Pt (fig 9) and LET samples with porous silicon/Ag (fig. 10) both show more stable and well-defined dependence of drain current on hydrogen peroxide concentration then samples without porous silicon (fig.11). Optimal conditions for concentration measurements are: U_{ds}=3..5 V, U_g=12 V (FET) or I_{LED}=20mA (LET)

All sensors have saturation of drain current from concentrations of hydrogen peroxide about 0.5-1% (fig. 14) and dependence on concentration is first order exponential decay $y = ae^{-\frac{x}{b}} + c$, obviously due to saturation of working area by reaction products or heating effect of hydrogen peroxide decomposition.

In concentration range up to 0.3% H_2O_2 best sensitivity was demonstrated by LET sensor (574 μA/%), for FET sensor sensitivity is about 6 μA/% for MISFET without active area and about 8.3 μA/% for MISFET with active area.

C. Time dependences

Time dependances of drain current allows to evaluate response time of sensor and influence of catalysts (fig. 13). As Ag and Pt catalyst H_2O_2 decomposition, sensors with metal nanoparticles shows quicker reaction (maximum response less than in 4 minutes). There is no significant difference between response time with Ag and Pt nanoparticles but signal of LET sensor with Ag nanoparticles remain more stable after maximum (deviation do not exceed 0.1%)

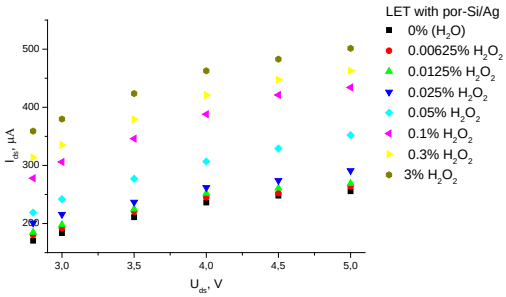

Fig. 10. Source-drain curves of LET with active area for different concentrations of H_2O_2

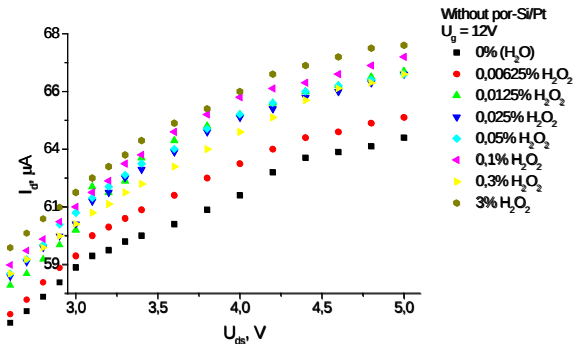

Fig. 11. Source-drain curves of MISFET without active area for different concentrations of H_2O_2

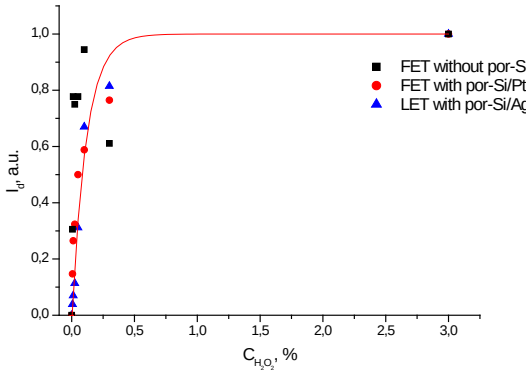

Fig. 12 Normalized source-drain current dependence on H_2O_2 concentration (Uds = 4 V, Ug= 12 V or ILED=20mA)

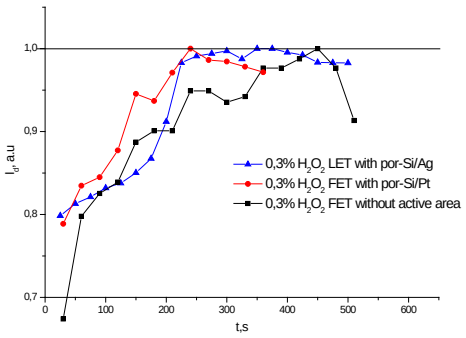

Fig. 13. Normalized source-drain current dependence on time at H_2O_2 concentration 0.3% (Uds = 4 V, Ug= 12 V or ILED=20mA)

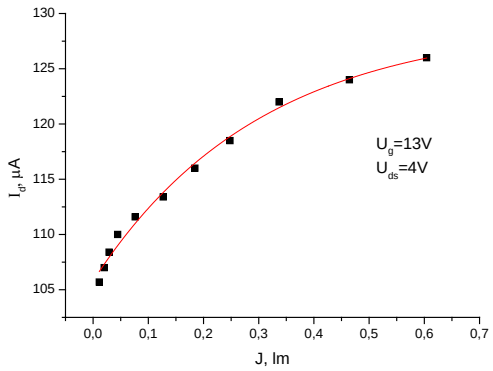

Fig. 14. Drain current dependece on luminous flux of MISFET with active area

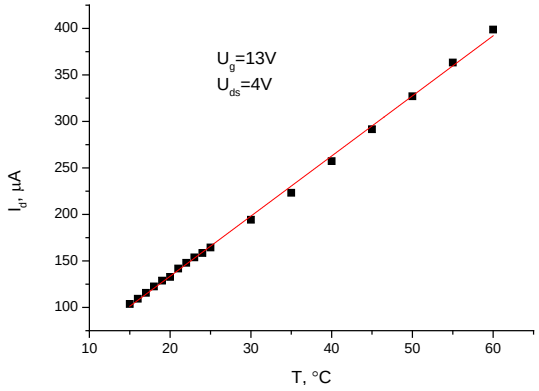

Fig. 15. Drain current dependece on temperature of MISFET with active area

D. Temperature and illumination dependences

To ensure accuracy and precision of measurements temperature and illumination of active area dependences of drain current should be taken into account. For in-field sensors temperature sensor should be incorporated into structure and measurements must be performed in dark.

MISFET with porous silicon demonstrates typical for silicon structures exponential decay dependence of drain current on luminous flux (fig. 14) and quasi-linear dependence on temperature (fig. 15). Slopes are 34 μA/lm and 6.46 μA/˚C respectively.

CONCLUSION

Both MISFET and as LET structures can be used as hydrogen peroxide sensor. Use of both Ag and Pt nanoparticles decrease response time of sensor to 2-3 minutes. MISFET structure with Pt nanoparticles is more controlled by gate voltage but have lower sensitivity (about 8 μA/%) and time stability (up to 0.2%); while LET structure is more simple, stable and sensitive (up to 500 μA/%). Further investigation is needed to clarify is this difference is due to sensor structure or to nanoparticles material.

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Сенсори на польових та фототранзисторах з металевими наночастинками та пористим кремнієм

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***Реферат*—В статті досліджуються два типи сенсорів перекису водню – на основі польового транзистора та на основі фото транзистора. В обох випадках чутлива область розташовувалась на тильній стороні кремнієвої підкладки і складалася з шару пористого кремнію з наночастинками металів (платини або срібла). Пористий шар отримувався шляхом хімічного травлення в присутності металів. Сенсори з пористим кремнієм демонструють достатню чутливість в обох конфігураціях. Польова структура є більш керованою, проте має нижчу чутливість (8 μA/%), тоді як фототранзисторна структура є більш простою та чутливою (до 500 μA/%). Використання срібних та платинових наночастинок зменшує час відгуку сенсора до 2-3 хвилин.**

Бібл. 21, рис. 15.

Ключові слова — пористий кремній; МДН-транзистор; фототранзистор; наночастинки срібла; наночастинки платини

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Сенсоры на полевих та фототранзисторах с металлическими наночастицами та пористым кремнием

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***Реферат*—В статье исследуется два типа сенсоров перекиси водовода – на основе полевого транзистора и на основе фототрензистора. В обеих случаях чувствительная область расположена на тыльной стороне кремниевой подкладки и состояла из слоя пористого кремния с наночастичками металлов (платины или серебра). Пористый слой был получен путем химического травления в присутствии металлов. Сенсоры с пористым кремнием демонстрируют достаточную чувствительность в обеих конфигурациях. Полевая структура болем управляема, но имеет болем низкую чувствительность (8 μA/%), тогда как фотостранзисторная структура более простая и чувствительна (до 500 μA/%). Использование серебряных и платинових наночастиц уменьшает время отклика сенсора до 2-3 минут.**

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Ключевые слова — пористый кремний; МДП-транзистор; фототранзистор; наночастички сребра; наночастички платины