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INVESTIGATION OF POROUS SILICON PHOTOCONDUCTIVE STRUCTURES

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Porous silicon layers photoconductive and electrical properties obtained by electrochemical etching of silicon have been investigated. Photoconductive and current-voltage properties depend on structure morphology are determined by not only properties of modified layer, but presence of charge carriers' traps. The photosensitivity of structures with PS layers is determined by thickness of porous layer.

Key words: porous silicon; sensor; photoconductivity; current-voltage characteristic; photosensitivity.

At a present time, the problem of controlling toxic and other harmful substances in the air atmosphere, drinking water, foodstuffs, etc. expected immediate solving. Thereby, there is a necessity for the development of microelectronic gas detection systems for industrial, office and residential apartment, which can be components of integral systems for protecting human life and health. Sensors based on nanoporous semiconductors, in particular, porous silicon (PS) are attracting special attention.

A set of optical sensors are described in a number of scientific papers [1-6]. Among such sensors we can separate photosensitive structures on porous silicon, based on the change of photoconductivity and its kinetics under the influence of various gas media, which can be used as effective gas analyzers. To design such sensors, it is necessary to know the dependences of the porous silicon photoconductivity on the state of the surface, which depends on the gas environment in which it is located, as well as the degree of the material porosity, the pores geometry and the frequency of modulation of the incident light intensity.

The porous silicon (PS) is predisposing the attention of researchers mostly due to its luminescent properties [2]. That is, since as in the layers of the PS was detected photoluminescence (PL) with a high quantum efficient at room temperature, this material became the object of intense both fundamental and applied research. Such a widely broad study of various properties of the PS has opened prospects for its numerous alternative applications in areas such as solar cells, biotechnology, sensors [1,8-9].

PS is a promising material for silicon electronics to creating gas and liquid sensors through a combination of crystalline structures and the giant external surface (200-500 m^2/cm^3) [3-4]. Effect of adsorption phenomena on the photoconductivity and current-voltage characteristics of PS structures are at the stage of initial studies with following practical application,

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based on the fact that the sensors are analytical tools for the analysis of solutions thanks to such characteristics as the express analysis, the ability of miniaturization and automation, simplicity their use and low cost.

Results of adsorption influence on electrophysic properties occur in the heterostructures formed on porous silicon based on silicon substrates of different types of conductivity under reaction of environmental hydrogen containing molecules (acetone $(CH_3)_2CO$, toluene (methylbenzene) C_6H_5-$CH_3C_2H_5OH$, benzene C_6H_6) are presented.

Gas molecules adsorption leads to the surface photoconductors recombination speed enhancing by increasing the charge carriers capture on energy trap levels is caused by adsorbed atoms, as well as the change in the structure of Si-Si "dangling" bonds. The intensity of photoconductors recombination at small gas concentrations is proportional to the partial pressure of the adsorbed exhaust and depends on its dipole moment. Molecules of adsorbate with a large dipole moment amplify the capture of electrons (holes) at the trap energy levels, which leads to an increase in the rate of recombination through these levels and changes the magnitude of photoconductivity. Thus, the effect of changing the photoconductivity of porous silicon under the influence of adsorbed gases is promising for the creation of effective gas sensors.

To produce samples by electrochemical etching a set of single crystal silicon wafers obtained by zone melting were used with crystallographic orientation (100) and (111). PS layers were grown directly on silicon substrates of p- and n- type doping with a resistivity of 0.01 to 10 Ω • cm.

PS layers growing carried out by electrochemical anodizing silicon crystal substrates in electrolytes based on hydrofluoric acid (HF). Ethanol solution of HF better penetrate inside the pores, which is very important for the horizontal layer uniformity in depth of PS crystal.

For electrophysical investigation the set of PS electrochemically etched samples were selected PS-nSi (n-type silicon doped sulphur substrate marked KES-0.01 and KES-4.5, $j = 35$ mA/cm^2, $t = 50$ min).

Etched substrates were separated on the single samples of 1 cm^2 square approximately. For establishing conductive properties of PS the three-point contact scheme was applied. Contact to the porous layer and back side about 2 mm in diameter was obtained by electrically conductive graphite varnish or glue. Current-voltage curves were obtained by PS surface in planar mode.

Measuring cell for all kind of PS properties investigations was constructed with possibility of input-output complicated vapour and gaseous mixture and external irradiation.

Current-voltage characteristics (CVC) of samples were measured at air environment. Time of measurement was about 5 minutes. All measurements were provided in the planar mode (on the surface of porous samples) on automatic equipment based on micro device controlling with capability of programming control. The set of experimental curves were measured by applying on the structure constant external bias supply at -15 - +15 V with a rate 100 mV/s, sampling interval was 0.2 s, save interval was 0.2 s. Current range was set in auto ranging mode as 10 nA – 10 mA. Signal was fixed under normal conditions in a parallel circuit measurement. For eliminating the influence of light, measurements were carried out in the dark.

For research porous silicon sensor structures dependencies, we used the measuring device E7-22 RLC-meter, voltmeter V7-21A, bridge resistances. Electric supply was applied from a source of constant tension B5-45. As voltmeter and ampermeter used combined digital multimeters.

For obtaining of PS photoconductivity spectral dependencies, the sample was contained in the measuring cell without substrate heating, and all measurements were carried out at room temperature and under normal environmental conditions. The main PS photoconductivity investigation scheme consists of a diffraction monochromator, amplifier, light source, registering device.

The modulating system is applying for photosensitivity investigations. All photosensitive spectral dependencies were conducted on the spectrophotometric measuring installation based MDR-12. Lightning system consist of light source, condenser system, spectral device, mechanical modulator. A 100W Tungsten halogen lamp integrated with convex ellipsoidal mirror with maximum at the near IR was used as the photon beam source.

The study of the PS sample surface morphology was carried out a scanning electron microscope REEMA-102-02 and on scanning probe microscope SolverNEXT with nanoindenter Solver NexT, NT-MDT, by atomic force microscopy (AFM) technique at the semi-contact mode in the air.

Fig. 1 presents the plan view SEM micrographs of PS prepared on the substrate of n-type conductivity KES-0.01 (PS-nSi), obtained with a scanning electron microscope REEMA-102-02. Flat crystalline silicon substrate surface have a look like mirror due to the manufacturing polishing. PS layer after electrochemical anodization in the plan-view the sponge-like islands macroarray of 200-200 nm sizes is clearly observed. Colour surface after electrochemical etching is dark with yellow contrast. This form of PS surface has such pore shape depends on orientation of silicon wafer and the way of electrochemical dissolution. Cross-section scan electron image confirm that the PS layer has sponge-shaped disordered etched pores. The thickness for porous orientation was about 20 μm.

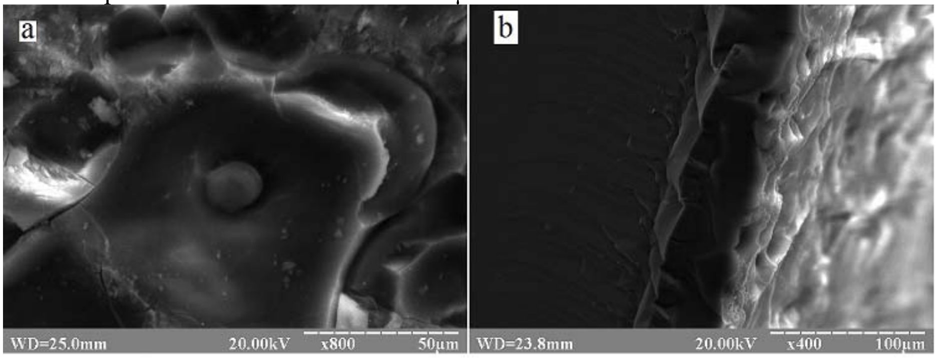

Fig. 1. a) PS-nSi scanning electron surface image,
b) PS-nSi cross-section scanning electron surface image.

Fig. 2 shows the surface of the PS on the substrate of n-type conductivity KEF-4.5. PS is matte and dark and there is clearly square-like macroarray structure surface with quadrate network of 200-200 nm size. Colour surface after electrochemical etching is dark. At a first look, the PS surface seems to be not too etched to form porous layer. But we observe the tendency of silicon nanowires forming among crystallographic axes of silicon wafer. The characteristic faceted, square shaped pores illustrate an orientation dependence of the photo anodization process of the Si (111) material, probably due to the anisotropy of Si (111) dissolution. The thickness for porous (111) layer was around 1 μm.

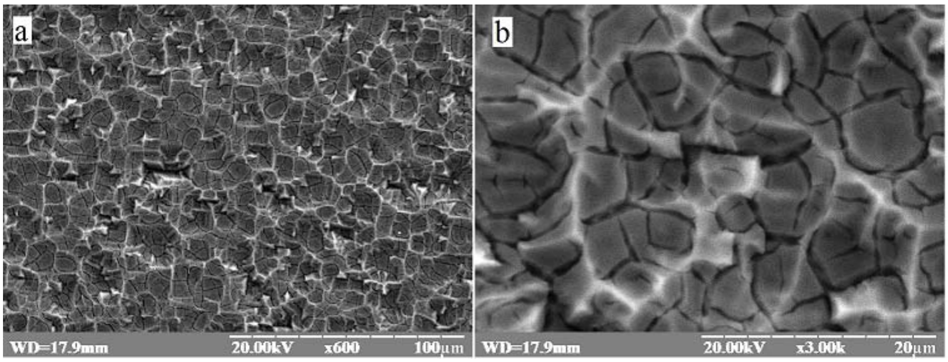

Fig. 2. a) PS-nSi (111) scanning electron surface image (600*), b) PS-nSi 111) scanning electron surface image (3000*).

PS sample surface morphology was carried on scanning probe microscope. The images seen on fig. 3 obtained by atomic force microscopy give possibility to observe square-like structure with forming an island of etched silicon substrate. Explanation of such porous surface growth tendency is caused by a huge etching time with electrolyte heating and surface penetrating.

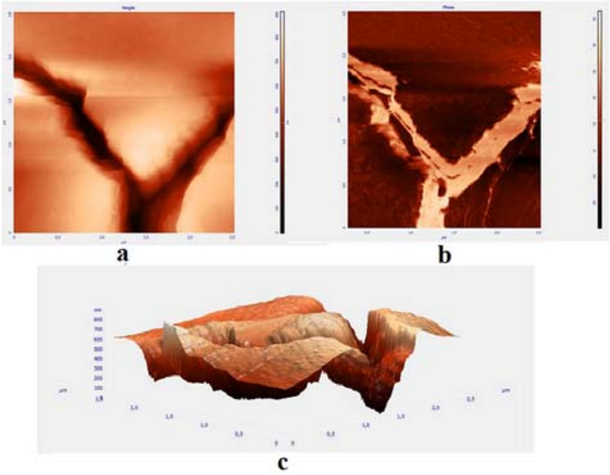

Fig. 3. PS-nSi scanning probe microscope image in next regimes: a) 2D-topography; b) phase contrast, c) 3D-image

Analysis of PS surface studies of etched samples and comparison with literature data, lead to the conclusion that the origin of cracks, islands, protrusions and cells on the PS surface is due to the emergence and formation of silicon ledge formed on the surface of crystalline silicon under the PS layer of the material of the silicon substrate during the etching.

Fig. 4 represents dynamic PS-nSi current-voltage curves, measured to establish an effective range for photoconductivity registration. The structure of current-voltage curves has a rectifying character, and there is no saturation of either direct or reverse current. The reverse current increases with increasing bias, and the direct is extrapolated by exponential dependence.

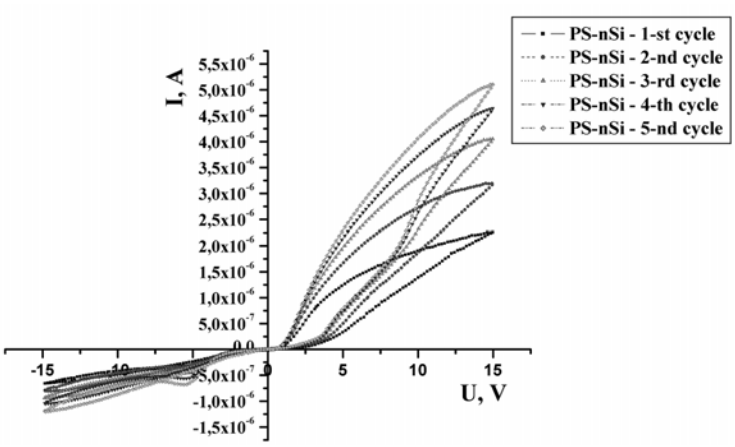

Fig. 4. PS-nSi structure dynamic current-voltage characteristic

Hysteresis loops were observed on dynamic current-voltage characteristic, measured with a low frequency step, indicating that the holes were captured on the traps. The typical times of direct and reverse current setting at pulse shift were respectively 40 and 13 s. This indicates a presence of slow traps [11, 12].

Fig. 5 shows the time dependencies of the current output with the applied external bias of +5 V.

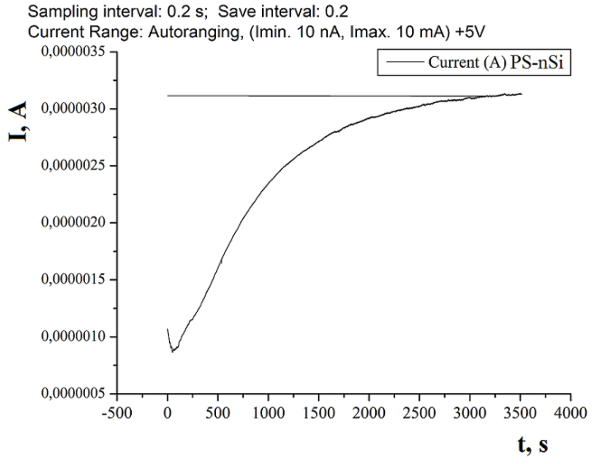

Fig. 5. Current output time dependencies under external bias +5 V.

As can be seen in fig. 5, under natural light and under normal atmospheric conditions, the time dependences of the current output at the applied external tension of +5 V indicate a considerable time to reach a stable state of electrons fulfilling due external tension and the instability of the spectral dependences of the photoconductivity.

Fig. 6 shows the spectral dependence of the PS-nSi photoconductivity with a thickness of about 20 µm, where the sample was oriented toward the light porous surface. Investigation of the photoelectric properties of PS layers on the silicon substrate is complicated by the fact that the absorbed radiation penetrates the PS layers into the silicon wafer.

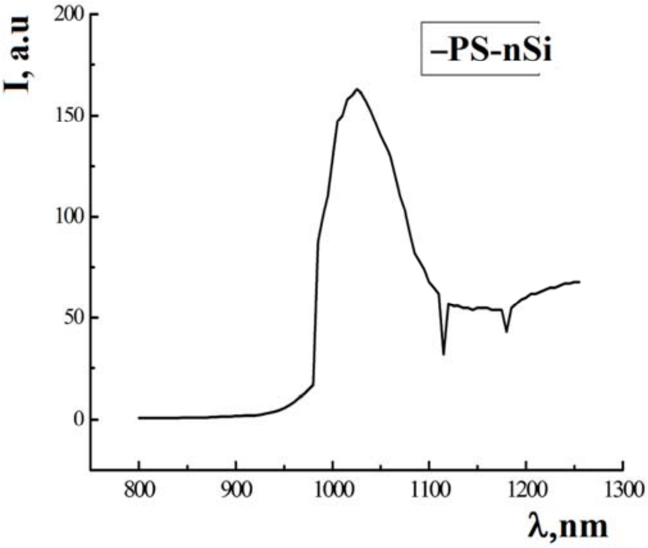

Fig. 6. PS-nSi photoconductivity at the room temperature (U=+8 V)

At the value of the applied voltage + 8V, the spectrum of the photoconductivity has a maximum current output of approximately the value of the applied voltage of order 10^{-10} A with the precision to the applied bias. However, in the photoconduction spectrum, flash flares of charge relaxation are observed at + 8V in the direction of reduction of current. The maximum is at 1045 nm, the region of spectral dependence 800-1200 nm.

Such photoconductive properties can be explained by processes of charge carrier generation under the influence of light. In the case of studying the n-doped silicon substrate, the carriers generated in the PS are recombined near the boundary of the charge spatial division region. The direction of the current depends on the value of the applied voltage. This affects the depth of light penetration into the PS-nSi structure and the depths of the levels where the carriers originate. Radiation with less energy results in photoconductive generation at deeper levels and before the partition of carriers on the PS-nSi barrier, depending on the applied field. The PS is transparent to light – the sensitivity spectrum is associated with generation charges in Si, not PS, and their recombination at the boundary of the PS-nSi. The light passes into the PS layer, in a wide geometric range. This light releases charges from traps of the Si substrate levels, and it plays a key role in the flow of current.

The presence of thick layers of PS on silicon substrate type KES-0.01 showed the presence of a change in the current conductivity signal only in the visible area of 500-800 nm. One of the peculiarity is the presence of a spectral dependence of conductivity in the region with a maximum at 650 nm.

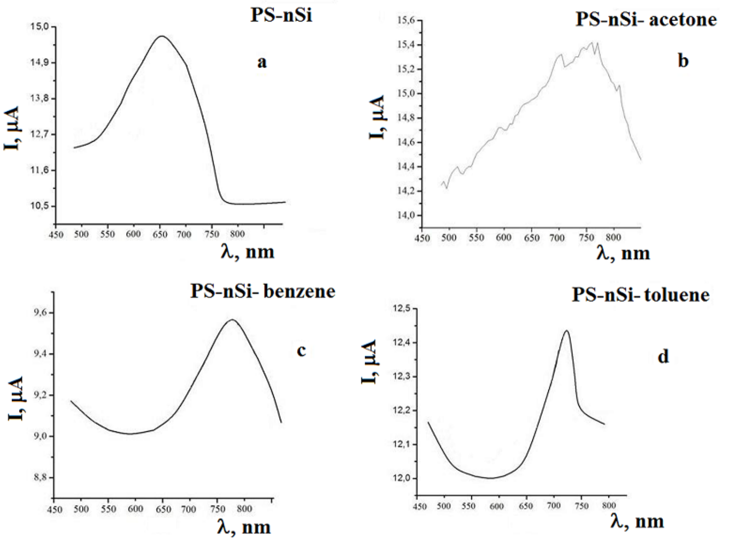

Fig. 7. PS photoconductivity at room temperature: a) normal atmospheric conditions; b) atmosphere of acetone vapor; c) atmosphere of benzene vapor; d) atmosphere of toluene vapors.

Therefore, an attempt was made the measurement of conductivity spectral dependence at the presence of harmful hydrocarbon compounds in the vapor environment. Fig. 7, b shows the spectra of the photoconductivity for PS acetone vapor content of 3.17 ppm. There is a shift in the maximum sensitivity for small signals for the test sample in the region of 760 nm. This can be explained by the adsorption of acetone molecules on the PS surface. At the presence of benzene vapor (2.61 ppm), reduction of conductivity can be explained by passivation of PS surface 'dangling' bonds by benzene rings, which leads to the appearance of additional traps on the surface of the investigated structure. Toluene evaporation (3 ppm) in a closed air volume resulted in a shift in the maximum band of the photoconductivity to a region of 730 nm and a decrease in the current output with the probability of passivation of the surface bonds of the PS. In addition, the toluene molecules act as acceptors. This explains the decrease in photoconductivity.

Due to the photosensitivity of porous silicon surface based on morphology and current-voltage characteristics, the investigated object can be applied as a gas sensor of harmful environmental gas due to the complicated and branched surface of the investigated structure. Photoconductive properties can be explained by processes of charge carrier generation under the influence of light. The presence of harmful hydrocarbon compounds in the vapour environment with definite content is leading to a shifting of the sensitivity maximum. This can be explained by the adsorption and influence of polarized hydrocarbon molecules on the PS surface properties.

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ДОСЛІДЖЕННЯ ФОТОПРОВІДНОСТІ СТРУКТУР НА ОСНОВІ ПОРУВАТОГО КРЕМНІЮ

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На сьогоднішній день виникає необхідність в розробці мікроелектронних систем детектування газів для промислових, офісних та житлових приміщень, які можуть бути компонентами інтегральних систем захисту життя і здоров'я людини. Особливий інтерес представляють сенсори на основі нанопоруватих напівпровідників, зокрема, поруватого кремнію. Для проектування таких сенсорів необхідно знати залежності фотопровідності поруватого кремнію від стану поверхні, що залежить від газового середовища, в якому він знаходиться, а також ступеня поруватості матеріалу, геометрії пор і частоти модуляції інтенсивності падаючого світла.

В даній роботі приводяться результати досліджень вольт-амперних характеристик, фотопровідності, які виникають в гетероструктурах, сформованих на основі ПК на кремнієвих підкладках різного типу провідності, при адсорбції водневомістких молекул (ацетон $(CH_3)_2CO$, бензол C_6H_6, толуол (метилбензол) C_6H_5-$CH_3C_2H_5OH$), а також кривих ВАХ при дії екологічних газів.

Дослідження морфології поверхні зразків поруватого кремнію на кремнієвій підкладці n-типу провідності проводились за допомогою скануючого електронного мікроскопа РЕЕМА-102-02 та на скануючому зондовому мікроскопі SolverNEXTз наноіндентером Solver NexT, NT-MDT, методом атомно-силової мікроскопії (АСМ) в напівконтактній моді на повітрі.

Представлено динамічні вольт-амперні характеристики, виміряні з метою встановлення ефективної області для реєстрації фотопровідності. Вольт-амперні характеристики структури має випрямляючий характер, причому не спостерігається насичення ані прямого, ані зворотного струму.

У випадку дослідження фотопровідності, генеровані в поруватому кремнії носії рекомбінують поблизу межі області просторового розділення зарядів. Наявність товстих шарів ПК на кремнієвій підкладці n-типу провідності, показала наявність зміни сигналу провідності по струму у видимій області 500-800 нм. Представлено спектральні залежності провідності при наявності в атмосфері парів шкідливих вуглеводневих сполук із фіксованим вмістом домішок. Спостерігається зсув максимуму чутливості при невеликих сигналах для досліджуваного зразка в області 650-850 нм.

Приведені експериментальні результати показують можливість застосування ПК як приклад застосування детектора шкідливих екологічних газів завдяки складній і розгалуженій поверхні досліджуваної структури.

Ключові слова: поруватий кремній; сенсор; фотопровідність; вольт-амперна характеристика; фоточутливість.

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