Silicon Structures with Variable Morphology of Pores Methods of Obtaining Physical and Optical Properties

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This paper presents experimental results on the creation of porous silicon structures with variable pore morphology (GPS-var). At a pore depth of up to several hundred microns, the structures are characterized by the presence of a layer with nanoscale porous structures (hereinafter, nanoporous) on the surface. As the depth of etching increases, the pores smoothly transform into spongy, and then into a columnar structures with pore sizes of about a micron.

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Porous silicon (PS) is a material that, as a rule, forms on the surface of single-crystal silicon wafers as a result of their chemical or electrochemical treatment in solutions based on hydrofluoric acid.1,2 As a result of anodic etching, selective etching of silicon and the formation of an array of channels or pores separated from each other by single-crystal walls forming a peculiar skeleton occur simultaneously at the same time on the entire surface. The cross-section of the channels, as well as the dimensions and shape of the walls between the pores, can vary from a few angstroms to several tens of microns and have different configurations and relative positions depending on the characteristics of the silicon, the composition of the electrolyte and the conditions of the etching process. In addition, the chemical disproportionation reaction accompanying the formation of pores during anodic etching is characterized by the partial deposition of silicon atoms on the surface and pore walls. In this case, various nanostructured layers are formed, which can have a significant effect on the properties of porous structures. The acquisition of a PS is compatible with the processes of silicon technology of manufacturing modern integrated circuits. A fairly simple possibility of a controlled change in the morphology of porous structures and their diversity determines the difference in the physical characteristics of the porous material, which ultimately determine one or another practical application of the PS.1

The interest for practical use is associated with nanoscale porous structures. It should be noted that the ratio of the volume of the etched and the remaining part of the silicon matrix, which is commonly called the porosity of the material, has a significant effect on the physical characteristics of the PS. With increasing porosity, nanoscale layers have increasingly different properties from silicon.4 Therefore, for porosity less than 10% with a pore diameter of not more than 1 nm, there are no noticeable changes, for example, optical properties of the material do not occur. At the same time, for PS with a porosity of more than 70%, effective photo- and electroluminescence is observed even at room temperature. The width of the forbidden band and the refractive index also change. Therefore, nanoscale structures can be used in IR-band optics as photonic crystals, Bragg reflectors in the case of the formation of strictly periodic porosity of the PS structure.5

When creating periodic structures with a local change in porosity (for example, the thickness of one of the layers), waveguide or resonator structures can also be realized. Nanostructured layers are characterized by a high surface area, which, depending on the porosity, can reach 1000 m²/cm³. This property is widely used to create various sensors and sensor devices. In addition to these advantageous structural characteristics, the PS is also a biocompatible material. In contrast to bulk silicon, the PS undergoes hydrolysis at room temperatures already in slightly alkaline (pH ~ 7.5) media, which makes it possible for its biodegradation in living organisms. Therefore, nanoporous silicon is very important for the development of nanoscale applications, such as molecular separation, biosensitivity, controlled delivery of drugs to the body and tissue engineering.1,4,6

Of great interest is the development and research of stable and reproducible membranes capable of separating molecules by size.4 The process of creating freestanding or self-supporting PS membranes usually involves several stages. First of all, formation of a PS layer with a controlled pore morphology is carried out on a silicon wafer. Pore sizes in terms of diameters and depth, should be commensurate with the size of the molecules necessary for filtration. In Ref. 4, the authors demonstrated layers with a pore scatter in diameter from 2 nm to 20 nm, with an average value of ~12 nm. In the second stage, the porous layer is separated from the silicon substrate. It was shown that for this purpose, the dependence of the pore diameter on the ingredient composition of the electrolyte or the change in the anode current density during the etching process can be used.7 By increasing the diameter at the bottom in such a way that there is a continuous overlap of the adjacent pores, it is possible to separate the porous layer from the substrate.8 Using these methods, membranes with a diameter of 1.5 cm and a thickness of up to 75 μm were formed.4 It should be noted that membranes formed in this way are characterized by high brittleness, which is related to the strength characteristics of the PS. The magnitude of the Young’s modulus decreases significantly with increasing porosity. So, if the Young’s modulus is 160 GPa for monocrystalline silicon, then for a PS with a porosity of 90%, its value drops to 0.87 GPa.9 Therefore, “free” nanoporous membranes must be fixed on a special holder. This significantly reduces the working area of the membrane. In Ref. 4, the authors used a holder of mica, to which a nanoporous membrane was fixed using epoxy glue. The working area of the membrane, at the same time, decreased from 1.767cm² to 0.05cm², which corresponded to the hole in the holder with a diameter of ~0.25 mm.

In this work, we propose a technique for manufacturing nanoporous membranes that are formed in a single anodic etching process on the surface of macroporous silicon. Processes have been developed for the formation of a gradient-porous silicon structure with variable pore morphology (GPS-var structure).10–13 The outer layer of the membrane based on the GPS-var structure is a nanoporous layer up to a thickness of a few microns. It is located on the sponge skeleton of the macroporous structure, which is not only a continuation of the nanoporous layer in depth, providing permeability for solution elements and gases, but also acts as a mechanical attachment of the nanolayer and, accordingly, provides acceptable strength of the composite. Particular attention is given to the consideration of practical problems, not only to preserve the nanoporous layer formed on the surface of the GPS-var membranes formed as a result of the anodic etching. A number of characteristics of the material have been investigated, which open up new possibilities for its application. In addition,
the proposed structural and technological solution allows more efficient use of the entire surface area of the porous membrane layer formed by deep anode etching of silicon wafers. The higher strength of the membrane, which does not imply the subsequent attachment of the nanoporous layer to the strengthening holder, allows the use of silicon membranes also as monolithic electrodes of micro fuel cell elements (μ-FC), which was experimentally demonstrated in Refs. 11–15, as well as electrodes of other currently sources.

Experimental or Theoretical

Gradient-porous silicon structures.—For the first time the term “gradient-porous silicon” (GPS) structures was used by us in work,10 which describes the creation of monolithic porous electrodes for μ-FC elements. One of the most important requirements for such electrodes is the provision of the required strength, which makes it possible to use sufficient force when attaching the electrodes to the proton-conducting membrane. In this case, the clamping force required for reliable electrical contact must be at least 200 N/cm².16 In addition, it is necessary to ensure the reliability of the electrical contact when operating under conditions of temperature and humidity changes in the “on-off” mode of the μ-FC.13–15 The multilayered GPS electrode structures had a macroporous structure consisting of alternating layers with columnar and spongy macroporous structures. The columnar pore structure was formed during anode etching in a solution of HF: C₃H₈O (ISO):H₂O = 6: 9: 25, and the sponge structure in the HF:C₂H₅OH = 1: 1 solution. The formation of the GPS structures proceeded at a constant density of the etching current. After the formation of the first layer, subsequent layers with a different morphology of pores were formed by replacing the ingredient composition of the electrolyte.10,13,14 The alternation of porous layers with different pore morphology made it possible to compensate for the arising mechanical stresses, both in the process of manufacturing electrodes of the required thickness, and in the conditions of their operation. After the formation of a multilayer PS layer with a depth of more than 200 μm, the remnants of the non-etched silicon were removed by mechanical grinding. The membranes thus produced were used as the basis for the subsequent formation of the anode structure and the cathode of the membrane unit of the μ-FC.17 The GPS membrane was successfully used as a reinforcing framework for encapsulation in the pores of the form of helium electrolyte. The helium-like electrolyte is a polyvinyl alcohol (PVA) esterified with phenol – 2,4-disulfonic acid (PSA). In the 4: 1 = PVA / PSA ratio, the electrolyte provides higher proton conductivity characteristics and, in addition, this electrolyte is up to 20 times cheaper than traditional Nafion membranes.17–20 A variety of design and technological characteristics and features of the use of membranes based on PS in the structure of the membrane-electrode block of μ-FC are described in detail in previously published papers.13,14,19 A disadvantage of electrodes based on macroporous GPS with a porosity of 50–60% is the low specific surface area of the working surface. Despite the presence of nanoscale (1–2 nm) pores on the surface of the wall in a layer with a thickness of 100 nm,21,22 no significant increase in the active surface area is observed. Efforts have been made to increase the specific surface area by depositing a layer of carbon nanotubes 20–50 nm in diameter on the inner surface of the pore walls. An increase in the specific surface area to 100 m²/g has been achieved.11,12 In addition, a significant (more than two orders) reduction in the electrical resistance of the electrodes was obtained. Such an increase in the active surface area of the electrodes, however, remains about an order of magnitude lower than the values typical for silicon nanoporous structures.1 Attempts to increase the thickness of the layer of nanofibers on the inner surface of the pores lead to cracking and destruction of the GPS membranes and do not provide an opportunity to create composite membranes based on GPS structures with nanofibrous carbon layers. Proceeding from the necessity to form the maximum specific membrane surface area, it is very attractive to study the possibility of creating porous membranes based on GPS-var structures, the outer layer of which is a nanoporous layer. The thickness of this layer can reach several microns, and its cross-section has a high limit of the specific surface area for porous silicon.

Formation of gradient-porous silicon structures with variable pore morphology in depth.—An essential feature of GPS-var membranes is the formation of an external nanoporous layer in the process of creating a deep porous structure with variable morphology, as well as the preservation of a nanoporous layer during the subsequent fabrication of membranes based on it. The chemical anodic etching (oxidation) of silicon in hydrofluoric acid is of a complex multi-stage
nature. The process is associated with a large number of consecutive and parallel reactions. The most important stages for the formation of a nanoporous layer are the processes described by the following reactions:

$$\text{Si} + 2h^+ + 2\text{HF} \rightarrow \text{SiF}_2 + 2\text{H}^+ \tag{1}$$

$$2\text{SiF}_2 + 2\text{HF} \rightarrow \text{Si} + (\text{SiF}_3)^2^- + 2\text{H}^+ \tag{2}$$

$$\text{SiF}_3 + 4\text{HF} \rightarrow (\text{SiF}_6)^2^- + \text{H}_2 + 2\text{H}^+ \tag{3}$$

$$\text{SiF}_2 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{HF} + 2\text{H}_2 \tag{4}$$

The first reaction describes the process of electrochemical interaction at the silicon-solution interface. The process takes place when there are positive charges on the surface. As such charge carriers in silicon are holes. This explains the fact that p-type silicon conductivity undergoes anodic oxidation without any additional external influences. In the case of silicon of the n-type conductivity, it is necessary, due to additional influences, for example the action of light, to ensure the influx of holes to the silicon-electrolyte interface. Reactions 2, 3, 4 describe oxidation-reduction processes taking place in the electrolyte which, to one degree or another, can also be stimulated by the surface of silicon itself and the porous layer, after its formation. In the latter case, this interaction increases substantially with the growth of the specific surface area in contact with the solution. Reaction 2 describes a disproportionation process that results in the precipitation of silicon atoms on the surface that form layers in an amorphous or crystalline form. Two other Reactions 3, 4, these are the oxidation reactions of silicon hypofluoride, describe processes competing with the process of disproportionation and, under certain conditions, can substantially influence it, up to complete suppression. Thus, when using a solution with a high water content, for example HF: ISO:H2O = 6:9:25, for the anodic etching, the process described by Reaction 4 predominates. Moreover, the nanoporous layer on the surface of the porous layer is not observed with the investigated silicon wafers p-type conductivity in a wide range of resistivity's. Therefore, to form deep GPS-var layers, one should use “anhydrous” electrolytes. In addition, the processing in the water should be excluded from the samples manufacturing process after the formation of the reinforced layer. To form the GPS-var structure, single-crystal silicon p-type conductivity wafers with a specific resistance of 10–80 Ω·cm, surface orientation (100) are used. The choice of the degree of doping of the original silicon makes it possible to form a supporting mesoporous layer with a skeleton wall thickness from hundreds of nanometers to microns. A silicon plate with a diameter of 100 mm and a thickness of 480 μm is divided into samples measuring 25 × 25 mm². The process of deep anodic etching is carried out in anhydrous solutions based on concentrated hydrofluoric acid and alcohol at a constant anode current density of 2.5–15 mA/cm². To improve the wetting of the silicon surface, cetyltrimethylammonium chloride (CTAC:CH₃(CH₂)₃N(CH₃)₃Cl) is added to the solution. The experimental results of the dependence of the etching rate on the depth of the porous layer in p-type silicon on the mass fraction of hydrofluoric acid in ethanol are presented in Figure 1 curve 3. The observed dependence is practically linear in nature and allows one to determine the composition of the electrolyte and the etching time for the production of porous silicon membranes of the required thickness. Electron microscopic studies of images of the transverse cleavage of GPS-var structures indicate the presence on the surface of a nanoporous layer with a thickness of up to several microns. This layer was observed both at small etching depths (less than 10 μm) and on samples with an etching depth of more than 200 μm. Replacement of ethanol by isopropanol, when changing from one solvent to another, character of the dependence of the rate of anodic etching in depth from the mass fraction of hydrofluoric acid. In the etching regimes considered, a porous structure with a variable pore morphology is also formed, but the dependence of the etching rate on the HF concentration is characterized by non-linearity (Fig. 1, curves 1 and 2). At the same time, the analysis of images in the scanning electron microscope (SEM) received by the GPS-var structures showed that at low concentrations of acid (up to 80%) during the etching process the nanoporous layer is cracked. The same phenomenon was observed by the authors of the work. The authors explained the destruction of the nanoporous layer by desorption or adsorption of moisture (water) during drying after washing, or holding the membranes in a moist air environment. In the case we are considering, a similar destruction of the porous layer is observed even without removing the samples from the solution at the end of the etching process. Figure 2a shows the SEM image of the GPS-var structure formed by anodic etching in a HF: ISO = 1:1 solution with the addition of a 10⁻³ M concentration of CTAC. Despite the relatively small thickness of the porous layer (~30 μm), cracking of the nanoporous layer occurred during etching, which was also detected by a jump in the voltage across the cell when monitoring the current-voltage characteristics of the anodic etching process. The destruction of the outer nanoporous layer is clearly seen in Fig. 2a. In the process of anodic etching in similar modes in a solution with an HF concentration of more than 80%, voltage jumps during the inspection of the current-voltage characteristics of the process are not fixed. At the same time, cracking of the outer layer is not observed, even at large thicknesses (~50 μm) of the porous layers (Fig. 2b). As already noted, the GPS-var structures as the nanoporous membranes are of great practical interest. To achieve these goals, it is necessary to form such a porous structure in depth, which makes it possible to create on its basis a membrane with the strength necessary for the subsequent application. Figure 3 shows the SEM image of an arbitrary fracture of a GPS-var structure with a depth of ~342 μm. The sample was formed in silicon wafer of the p-type conductivity. Specific resistance ρₜ = 80 Ω·cm, surface orientation (100). Solution based on HF: Cl₃H₃OH: CTAC = 200: 50: 1, etching current density 10 mA/cm². The surface layer is a nanoporous layer which, with increasing depth of etching, “smoothly” is transformed into a “spongy” structure of macropores and separating walls of a monocrystalline skeleton. The pores at the bottom of the layer in the process of further anodic etching under the action of developing mechanical stresses self-organize into a columnar structure (Fig. 3b) with a quasi-hexagonal topological arrangement.

![Figure 2](image-url)
Figure 3. SEM images of the transverse cleavage of the GPS-var structures. The inset shows an optical image characterizing the topological arrangement of columnar pores at the bottom of the porous membrane after removal of unsealed silicon.

Figure 3c shows the optical image of the surface of the membrane formed after removal by mechanical grinding of the lower uninfected layer of silicon. It is seen that the topology of columnar pores at the bottom of the layer has a hexagonal arrangement. The membranes formed in this way have sufficient strength, which allows not only to use the unique properties of the nanoporous layer located on the surface, but also to develop electrodes for μ-FC and other current sources on the basis of such a membrane (for example).

Results and Discussion

Analysis of the characteristics of the outer nanoporous layer of the GPS-var structure.—The process of precipitating Si from the solution on the surface of the pores can proceed with the formation of a crystalline or amorphous layer. Under the conditions of anodic etching, both these processes are thermodynamically favorable, but one is realized in which there is a minimum of the work of formation of the critical nucleus. Calculation of the kinetics of heterogeneous nucleation in the case of the anodic etching process is a complex problem with a lot of unknown parameters, therefore it is impossible to state unequivocally the realization of any one mechanism. The deposited layer of nanoporous silicon can be characterized only by studying the structure of the formed layer. Figure 4 shows the SEM image of the outer surface layer of the GPS-var structure formed by an anode silicon etching in a HF solution: ISO = 6:1 (with the addition of CTAC ~ 10^{-3}M) at an anodic current density of 10 mA/cm². The surface orientation of the wafers (100) with a resistivity of 40 Ω·cm (Figs. 4a, 4b, 4c) and 10 Ω·cm (Fig. 4d). The outer nanoporous layer of both samples is characterized by a relatively flat, planar surface. A significant difference is observed in the structure of the porous layers formed under the external nanoporous layer. For a higher-resistance sample, the boundary of the nanoporous layer and the supporting spongy skeleton located beneath it is characterized by considerable development and non-planarity of the surface (Figs. 4a, 4b, 4c). A flat nanoporous surface layer covering (filling) the developed surface of the skeleton is shown in Fig. 4b with an arrow. The layer is characterized by variable thickness from 1 to 3.5 μm. In some point-like places, a through distribution of fragments of the silicon skeleton (pore walls) through an external nanostructured layer can be observed. In the isometric image (Figure 4a), such areas of the surface are marked by arrows. For silicon with a resistance of 10 Ω·cm, a less thick but more plane-parallel structure of the surface nanolayer is characteristic. First of all, this is due to the flatter and homogeneous interface of this layer and the supporting mesoporous skeleton of the Investigation of the region of the surface nanoporous layer, marked with an arrow in Fig. 4b, was carried out by transmission electron microscopy (TEM). An analysis of the electron diffraction pattern of this layer indicates the amorphous structure and the absence of crys-
Figure 5. TEM analysis of superficial nanoscale GPS-var structure: a) TEM image of the surface nanolayer; b) electron diffraction pattern of the surface nanolayer.

talline elements in the structure, including the skeleton of the silicon substrate (Fig. 5b). The structure is characterized by a low density of the material with porous holes of diameter \( \sim 20 \) Å (Fig. 5a). These representations coincide with the results of analysis of the surface structure obtained by scanning atomic-force microscopy (AFM) methods. The three-dimensional AFM image clearly demonstrates that the surface image is a highly developed porous structure with pore sizes of 20–50 Å. As follows from this analysis, the roughness parameter of the considered region of the sample \( R_Z \) pore does not exceed 1 nm. The absence in the structure of the external nanoporous layer of the silicon skeleton of the substrate (with the crystal structure of the initial silicon substrate) indicates that the layer is formed in amorphous form mainly due to the disproportionation of silicon. At the same time, the precipitation of silicon from the solution takes place on the surface contacting with the solution, which also acts as a kind of catalyst for the disproportionation reaction process.27,28

Surface roughness was studied on a Talystep machine with Talydate-2000 computer processing. It was found that the degree of surface roughness change after anodic etching depends on the roughness of the initial surface of the silicon wafer. Thus, an increase in the \( R_Z \) parameter for a surface with an initial value of \( R_Z \) silicon = 1.85 nm occurred 8 times (\( R_Z \) pore/\( R_Z \) silicon = 14.8 nm/1.85 nm = 8). For a surface with a starting value of \( R_Z \) silicon = 20.13 nm, this increase was 2.3 times (\( R_Z \) pore/\( R_Z \) silicon = 46.29 nm/20.13 nm = 2.3). The data presented allow us to conclude that the presence of an experimentally established surface roughness (\( R_Z \) pore = 46.3 nm) is not technically difficult to form a continuous layer of various metals with a thickness of the order of 100–150 nm by practically all known vacuum deposition methods. This opens the possibility of creating separating palladium membranes for hydrogen purification. The performance of such membranes, other things being equal, is more than 1–2 orders of magnitude higher than the productivity of existing separating membranes with palladium films of thickness from one to tens of microns, since it is inversely proportional to the thickness of the separating layer of palladium.

Analysis of the composition of the nanoporous layer of the GPS-var structure was carried out with the help of SIMS and Ouger spectroscopy. SIMS analysis of the samples was carried out on an IMS-4f unit.29 The analysis was carried out with the help of primary \( \text{Cs}^+ \) ions. The primary beam scanning area was \( 250 \times 250 \) µm². Secondary ions were registered from the 40% central zone of the entire scanned area. The energies of the primary \( \text{Cs}^+ \) ions were 5.5 keV. The current of the primary \( \text{Cs}^+ \) ions were \( 4 \times 10^{-8} \) A. The vacuum in the sample region in the analysis was \( \sim 10^{-8} \) Torr, with the etching time of the sample of 80 min. Analysis of profiles of the relative intensity distribution of SIMS signals indicates a relatively higher concentration of hydrogen in the near-surface layer of the nanostructure. These data can serve as additional confirmation of the mechanism of anodic etching of silicon, according to which hydrogen released during the anodic etching passivates dangling bonds on the walls of the pores of the etching surface, forming Si-H bonds. A larger area of the specific surface corresponds to a higher concentration of hydrogen. The SIMS profile of hydrogen distribution indicates that the closer to the surface, the larger the specific surface area can be used to characterize the layer. In addition, at a depth of about 1 micron, enrichment

Figure 6. The experimental dependence of the reflection coefficient on the wavelength range 480–1200 nm of the membrane based on GPS silicon: a) on the front side b) on the back side.
with oxygen is observed. The presence of oxygen in the structure of the nanoporous GPS-var layer is also confirmed by Auger analysis. Depending on the energy used, the atomic oxygen content can reach 40.6%. According to Auger analysis, a significant presence of carbon was found (up to 30.7% atomic%) in our experiments. This is primarily due to the use of electrolyte structures based on alcohols and CTAC for the formation of GPS-var. The mechanism of the formation of the surface layer is accompanied by a disproportionation reaction. As a result, atomic silicon precipitates out of the electrolyte solution. A silicon layer with intrinsic electrical conductivity is formed on the surface, which is much lower than the conductivity of the doped silicon substrate. In addition, the oxygen observed in the structure may indicate the oxidation of silicon to some extent. Indeed, the surface resistance of the porous layer is (140–190) \Omega/sq.\textsuperscript{15}.

**Investigation of the anti-reflection properties of the surface of GPS-var membranes.**—The GPS-var membrane obtained by mechanically removing the silicon substrate to a thickness of 150 μm, formed by analogy with the membrane depicted in Fig. 3, was studied using spectrophotometry. The Agilent Technologies Cary 5000 spectrophotometer with automatic universal measuring set-top box UMA allows to measure transmission in the range of angles of incidence of light (0.0–90°) and mirror reflection in the range of angles of incidence (5.0–85°): diffuse scattering, reflection and transmission of light in the wavelength range 200–2500 nm with a minimum pitch at angles of 0.020, and also with s- and p-polarizations of incident light. The spectral dependence of the reflection coefficient of the membrane from the side (Fig. 6a) of the nanoporous layer and from the back side (Fig. 6b) of the membrane characterized by an extremely low value of the reflection coefficient, not exceeding 0.11%. In this case, the presence of a nanoporous layer approximately halves and this value of the reflection coefficient over the entire wavelength range.

**Summary**

1. A new technological design of membranes has been developed, where nanoporous layers are located on the surface of a macro-porous silicon skeleton. A feature of this version is that both the membrane and the supporting skeleton are formed in a single anodic etching process and do not require additional reinforcing skeletons for use in separating devices, as well as μ-FC electrodes and electrodes of other chemical devices.

2. The characteristics of a nanoporous membrane based on GPS-var structures were studied. Nanoporous layers of membranes are amorphous layers with pore sizes of several tens of angstroms. Membranes based on GPS-var structure are characterized by unique antireflection properties, the reflection coefficient does not exceed 0.11% in the whole investigated range of wavelengths of light.

3. The roughness of the layer formed on the face of the silicon plates does not exceed 20 nm, which makes it possible to use this surface to create ultra-thin continuous metallic layers on the nanopore surface.

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