Investigation optical properties and functional surface characteristics of nanoparticles based on porous silicon for applications in biomedicine

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Abstract. In this paper optical characteristics of porous silicon layers and nanoparticles are investigated. Samples were obtained by electrochemical anodic etching of n-type conductivity monocrystalline silicon wafers. It is shown that the surface morphology porous silicon samples are depending on etching technological parameters.

1. Introduction
Nowadays porous silicon (por-Si) is one of the perspective material in field of drug delivery system (DDS). Nanocontainers based on porous silicon have attractive properties as stability, ability to high loading, high biocompatibility and the prolonged release possibility of one, two or more drugs with different physico-chemical properties [1-3]. However, to enable loading and retention of useful drugs in the porous nanoparticles we are needing to know information about internal structure, morphology and surface chemistry of the delivery drug system. Determination of nanoparticles size and form is also an important task for DDS applications in vivo. Since it is expected that these characteristics will affect bioavailability, biodistribution of nanoparticles and their interaction with the cells of the body tissues [3-6].

Thus, it is necessary to investigate changes in composition, morphology and optical properties of porous silicon nanoparticles, depending on the method of their preparation for further application in medicine and pharmacology fields [7-13].

2. Experimental
In this work, porous silicon layers were obtained by electrochemical anodic etching of n-type conductivity monocrystalline silicon wafers with [100] crystal orientation. As electrolytes are used solutions based on hydrofluoric acid with added alcohol and dimethylformamide. Por-Si powders were obtained from meso, macro and nanoporous silicon samples by using ultrasonic bath (5 min, 100 W, 35 kHz). The transmission electron microscopy powders’ results are shown in Figure 1, 2.
Figure 1. TEM image of the surface of a) "mesoporous" – serial number 1 b) "macroporous" – serial number 2 silicon powder.

Figure 2. TEM image of the surface of "nanoporous" – serial number 3 silicon powder.

The conditions for obtaining porous silicon samples are presented in Table 1. As can be seen from Table 1 the technological parameters varied during the electrochemical process were the current density and the anodizing time, the composition of electrolyte.

Table 1. Technological parameters of electrochemical etching.

| Serial number of samples | Resistivity, $\Omega \cdot$cm | Electrolyte composition | Anodizing time, min | Anodization current density, mA/cm$^2$ |
|--------------------------|-----------------------------|-------------------------|---------------------|---------------------------------------|
| 1                        | 0.2                         | HF:C$_3$H$_6$O$_2$H$_2$O$_2$ | 10                  | 25                                    |
| 2                        | 0.2                         | HF:C$_3$H$_6$O$_2$H$_2$O: (CH$_3$)$_2$NCOH | 10                  | 25                                    |
| 3                        | 1                           | HF:C$_3$H$_6$O$_2$H$_2$O$_2$ | 10                  | 70                                    |
Porous silicon layer surface composition was analyzed using infrared Fourier-transform spectrometer Vertex 70 (Bruker) with console for spectroscopy of disturbed total internal reflection (measurement range 4000-550 cm\(^{-1}\), resolution 2 cm\(^{-1}\)). Analysis estimated depth of this method at wavenumbers up to 2000 cm\(^{-1}\) is limited to 1.5 \(\mu\)m, and in the range 2000-4000 cm\(^{-1}\) does not exceed 10 \(\mu\)m.

3. Results and discussion

Porous silicon powders, obtained under various electrochemical etching technological conditions, were investigated using Fourier-transform spectroscopy method. IR transmission spectra of nano-, meso- and macroporous (macro-) porous silicon nanoparticle powders is represented at Figure 3.

![Figure 3. IR-transmission spectra of porous silicon nanoparticle samples for various series: a) series 3 nano por-Si b) series 1 meso por-Si c) series 2 macro por-Si](image)

As seen from the spectra, all samples are characterized by sufficient number of Si-Si bonds valence symmetric vibrations (frequency 616 cm\(^{-1}\)), SiO valence antisymmetric vibrations in O-SiO and C in C-SiO (frequencies 1060, 1130, 1075 cm\(^{-1}\) for nano-, meso-, macro por-Si, respectively). Since the porous silicon nanoparticles surface is highly developed (powders specific surface area reaches 700 m\(^2\)/g), and there are hydrogen-containing components (HF, C\(_3\)H\(_8\)O) during the process of production and storage, all samples have adsorbed hydrogen, which forms bonds with silicon atoms in various forms (frequencies 800 cm\(^{-1}\) SiH\(_2\) twisting, 870 and 890 cm\(^{-1}\) – scissor).

A noticeable presence of antisymmetric deformation bonds CH\(_3\) vibrations at frequencies 1470 cm\(^{-1}\) for samples of series 2 and 3, as well as the valence antisymmetric CH bonds vibrations in CH, CH\(_2\) at frequencies 2859, 2916 cm\(^{-1}\) for macro- and mesoporous silicon samples only, allows to make
a conclusion about the dispersion storage medium influence (isopropyl alcohol) on the CH₃ complexes formation on the nanoparticles surface of all samples.

4. Summary
In this work, three series of porous silicon samples were obtained by electrochemical anodic etching. As electrolytes are used solutions based on hydrofluoric acid with added alcohol and dimethylformamide. Porous silicon powders were obtained from meso, macro and nanoporous silicon samples by using crushing in ultrasonic bath.

Electrolyte with N,N-Dimethylformamide addition (samples of series 1 and 2 comparison) allows to form larger porous silicon nanoparticles due to the fluoride ions decreased concentration in the solution. An increase in anodization current density leads to a decrease in the size of the porous silicon nanoparticles to the nanometer scale (sample of series 3).

From the analysis of infrared Fourier-transform spectroscopy data, it can be concluded that the samples surface of all series is passivated by oxygen and hydrogen molecules, which is explained by the presence of water and isopropyl alcohol in the electrolyte composition.

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