Investigation of the photoluminescence of porous silicon layers obtained under various technological conditions

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Abstract. The article considers the information about optical properties of porous silicon layers. Samples were obtained using electrochemical and photoelectrochemical anodic etching methods. The monocrystalline n-type (phosphorus doping) silicon was used as the initial material for preparation. It is shown, that the photoluminescence intensity and wavelength, surface morphology of porous silicon samples are hinge on many technological conditions. The results can be used to estimate an advisability of porous silicon particles application as biomarkers; LED and other optical devices creation.

1. Introduction
Porous silicon (PSi) is an essential material in terms of creating different devices, due to its various properties, which depend on many technological factors [1-4]. It is known, that there is a possibility to control material characteristics such as dielectric permeability, intensity and wavelength of luminescence, optical transmission and other. Thereby, one can take advantage of PSi as the material for photonics, optoelectronics, electronics, energetics and biomedical application. Thus, there is an opportunity to improve the efficiency of PSi layers and nanoparticles application in many areas by varying and combining technological conditions of preparation.

Silicon is a non-direct-gap semiconductor and its application as the material for LED devices is impractical because of inefficient luminescence. However, porous silicon layers, obtained by certain technological conditions, have an effective photoluminescence (in some cases – electroluminescence) in a visible, near ultraviolet and infrared range [5].

The investigation deals with the preparation conditions of photoluminescent PSi layers for biomedical purpose (targeted drug delivery, theranostics, etc). Special attention in the experiment is given to the hydrophilic/hydrophobic nature of porous layers. In previous works [6, 7] it is shown, that silicon nanoparticles must have hydrophilic properties of the surface for efficient drug encapsulation.

It is important to investigate the photoluminescence mechanism and spectrum of PSi layers for biomedical application. It has been revealed, that incident wavelength (in electrochemical etching process) results in change of surface parameters, morphology and skeleton distribution.

Thus, the study presents the investigation of preparation conditions (technological conditions) influence on obtaining biocompatible photoluminescent PSi layers, using electrochemical and photoelectrochemical anodic etching methods.
2. Experimental

Porous silicon samples were prepared using electrochemical and photoelectrochemical anodization (electrolyte – aqueous solution of hydrofluoric acid with addition of isopropyl alcohol). The monocrystalline n-type (phosphorus doping) silicon wafers were used as the initial material. The preparation conditions are represented in Table 1 and 2.

| Silicon parameters | Resistivity, Ω-cm | Anodization time, min | Anodization current density, mA/cm² |
|-------------------|-------------------|-----------------------|-----------------------------------|
| n-Si <111>        | 4.5               | 20                    | 20                                |
|                   |                   |                       | 40                                |
|                   |                   |                       | 60                                |
|                   |                   |                       | 80                                |

| Silicon parameters | Resistivity, Ω-cm | Anodization time, min | Incident wavelength, nm | Anodization current density, mA/cm² |
|-------------------|-------------------|-----------------------|-------------------------|-----------------------------------|
| n-Si <111>        | 4.5               | 20                    | 650                     | 20                                |
|                   |                   |                       |                         | 40                                |
|                   |                   |                       |                         | 60                                |
|                   |                   |                       |                         | 80                                |

It is shown, that the variable technological parameters of anodic etching are the current density and incident wavelength (presence or absence). Anodization time is constant – 20 minutes; incident power – 250 mW, wavelength – 650 nm.

The radiation source (laser) was used to generate more electron-hole pairs at the sample surface/electrolyte boundary, which directly stimulates the anodic dissolution process [8,9].

The spectra of the samples were studied by a spectrofluorimeter; the excitation wavelength of the photoluminescence of porous silicon layers is 405 nm.

3. Results and discussion

The experimental dependence of radiation intensity as a function of the photoluminescence wavelength for electrochemical (a) and photoelectrochemical (b) anodic etching is represented in Figure 1. As can be seen, the samples, obtained using photoelectrochemical etching technique, have more intensity photoluminescence in the shortwave region in comparison with the samples, obtained by electrochemical anodic etching. This phenomenon is connected with the intensification of various processes (dissolution, oxidization, etc) under the influence of light, which results in porosity, morphology and other parameters. The presence of additional peaks in the short-wavelength region, probably, is associated with various recombination mechanisms. The absence of a shift in the luminescence peak at a wavelength of 714 nm indicates that recombination occurs predominantly on structural defects. The samples, obtained by photoelectrochemical etching, have a peak at a wavelength of 644 nm, which we assume to be associated with a number of factors: the change in the dimensions of silicon nanocrystals, the contribution of recombination to the thermolysis of charge carriers.
Figure 1. Graph of the photoluminescence intensity as a function of the wavelength (a) – electrochemical etching, (b) – photoelectrochemical etching.

The experimental dependence of the photoluminescence intensity of porous silicon layers, obtained by photoelectrochemical anodic etching, as a function of the exposure time by a source of radiation (wavelength – 405 nm) is shown in Figure 2.

Figure 2. Graph of the photoluminescence intensity (of a single peak at ~700 nm) as a function of the exposure time.

As can be seen from the figure, the luminescence intensity of the samples decreases with increasing exposure time. This circumstance can be explained if one assumes that under radiation, the oxidation (on the air) of the sample occurs more rapidly, which directly affects the photoluminescence efficiency of the layers of porous silicon.

4. Summary
The samples, which were obtained by electrochemical and photoelectrochemical anodic etching at various current densities (20…80 mA/cm²) from initial monocrystalline silicon <111>, were studied. It is shown, that radiation, which is used in the process of photoelectrochemical etching, has a significant
contribution to the characteristics of the samples. It is assumed that the photoluminescence spectral band shift of the samples to the short-wavelength region is associated with a decrease in the size of silicon nanocrystals and electron thermolysis (the recombination mechanism). In both cases (electrochemical and photoelectrochemical etching), the peak at 714 nm is stable, which is connected with recombination on the defects. It should also be noted that the samples obtained by photoelectrochemical etching are characterized by more intense photoluminescence.

Thus, one can control porous silicon parameters (the radiation wavelength, the intensity of photoluminescence) by changing technological conditions of preparation (using illumination $\lambda = 650$ nm, which influences on the anodic side of silicon). These results are essential in terms of creating various light-emitting devices and methods, where PSi is used as luminophore (biomarkers, for example).

5. Acknowledgments
The work was carried out as part of the project event 5.1.2 “Increase of the publication activity of scientific and scientific-pedagogical workers” to increase competitiveness among the world's leading research and educational centers program.

6. References
[1] Canham L T 1990 Silicon Quantum Wire Array Fabrication by Electrochemical and Chemical Dissolution of Wafers Appl Phys lett (N) 57(10) pp 1046–1048
[2] Canham L T 1997 Properties of Porous Silicon EMIS datareview series (IEE Press London) lett (N) 18
[3] Spivak Yu M, Moshnikov V A, Pshchelko N S, Kadi Y S, Nalimova S S 2014 Morphological Feature Analysis of the Prospective Combined Gas Sensitive Sensor Elements Smart Nanocomposites vol 5 (1) p 5
[4] Moshnikov V A, Gracheva I E, Lenshin A S, Spivak Yu M, Anchkov M G, Kuznetsov V V, Olchowik J M 2012 Porous Silicon with Embedded Metal Oxides for Gas Sensing Applications Journal of Non-Crystalline solids vol 358 pp 590-595
[5] Korotcenkov G, Cho B K 2010 Silicon Porosification: State of the Art Critical reviews in solid state and materials sciences lett (N) 35:3 pp 153–260
[6] Pastukhov A I, Belorus A O, Bukina Ya V, Moshnikov V A, Spivak Yu M 2017 Influence Of Technology Conditions On The Surface Energy Of Porous Silicon Using The Method Of Contact Angle 2017 IEEE Conference of Russian Young Researchers in Electrical and Electronic Engineering (EICONRUS) pp 1183-1185
[7] Spivak Yu M, Belorus A O, Somov P A, Bespalova K A, Moshnikov V A, Tulenin S S 2015 Porous Silicon Nanoparticles for Targeted Drug Delivery: Structure and Morphology Journal of Physics: Conference Series vol 543 (1)
[8] Asano T, Higa K, Aoki S, Tonouchi M, Miyasato T 1992 Effects of Light Exposure During Anodization on Photoluminescence of Porous Si Jpn J Appl Phys lett (N) 31 (Part 2) p 373
[9] Föll H, Carstensen J, Foca E, Leisner M 2007 Understanding and Controlling Pore Etching in Semiconductors ECS Transactions pp 309-322