Some features of controlling the composition of a porous silicon surface with the use of “simplest” post-treatment techniques

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Abstract. The article is concerned with the investigation of techniques of the post-treatment of porous silicon. To study the features of changing the composition of the chemical bonds of the surface of porous silicon, we used the method of infrared spectroscopy.

1. Introduction
The complex composition of porous silicon surface including both crystalline and amorphous silicon, silicon dioxide and sub-oxides as well as adsorbed hydrogen and hydroxyl groups, is an advantage and at the same time a disadvantage of this material. On the one hand, a wide range of possible morphological and compositional characteristics opens up great possibilities for the utilization of porous silicon in a lot of applicable problems, but on the other hand, it creates problems in selecting a suitable technique for a particular practical application. In addition, this imposes restrictions on its storage conditions and subsequent technological operations with this material. For example, a number of studies are currently carried out in the field of material design to provide targeted drug delivery, in which researchers are trying to introduce porous silicon nanoparticles into living organisms or single cells. It is important to note that cells and organs do not experience the toxic effect of silicon particles [1-3]. The surface of these particles can be inoculated with molecules called bio-markers, which are used in the diagnostics of the analyzed cells, as well as medications used to restore impaired cell functions. However, the high surface activity of porous silicon that allows adsorption of certain active molecules on its surface, at the same time determines the instability of the surface properties of this material. Therefore, an important task when working with porous silicon and nanopowders based on this material is controllable stabilization and further functionalization of its surface. Thus, to solve these problems, thermal annealing of porous silicon in an oxygen medium, carbonization, and treatment with certain acids were proposed. However, these techniques are not applicable in the cases when the results of post-treatment lead to the formation of phases that are not characteristic of the source material, or to the appearance of new morphological features or adsorbed reaction products on the surface. For example, surface treatment at elevated temperature is known to result in the appearance of additional mechanical stresses in the porous layer and to its cracking. In turn, this can
result in a degradation of the quality for the films grown on the structure during further technological operations, or in a decrease in the size of the synthesized nanoparticles [4-7].

2. Experiment
Porous silicon samples were obtained by electrochemical etching of single-crystalline silicon of KEF (100) type with a resistivity of 0.2 Ohm·cm. A solution based on fluoric acid with the addition of isopropyl alcohol and hydrogen peroxide was used as an etchant for the ratio of the components of 2:2:1, respectively. The standard post-treatment of the samples applied for removal of reaction products and partial passivation of the surface included rinsing in distilled water and soaking in isopropyl alcohol for 5 minutes in both procedures.

Here we present investigations of the effect of the simplest or, in other words, “basic” techniques for the post-treatment of porous silicon on the composition of its surface without any temperature exposure or reactants that were not used to obtain porous silicon. The technique for the post-treatment of the surface was chosen on the basis of general ideas on the etching mechanism in obtaining porous silicon. Thus, to provide additional oxidation of the porous silicon surface according to the reaction Si + 2H₂O → SiO₂ + 2H₂, additional treatments were implemented by soaking in distilled water and a 30% solution of hydrogen peroxide. At the same time, to reduce the fraction of surface oxides according to the reaction SiO₂ + 6HF → H₂SiF₆ + 2H₂O, chemical sub-etching in an alcoholic solution of fluoric acid was selected as HF:C₃H₆OH 1:5. The production technique and the steps of the post-treatment are presented in detail in Table 1.

Table 1. The technique for obtaining the samples and the post-treatment parameters

| Series, designation | Type of the plate of single-crystalline silicon, current density, mA/cm² | Post-treatment, the order of the process, solution | Time of post-treatment over the steps, min. |
|--------------------|------------------------------------------------------------------------|-----------------------------------------------|------------------------------------------|
| 181, stand         |                                                                         | 1)H₂O 2) C₃H₆O                                 | 5+5                                      |
| 182, stand +H₂O    |                                                                         | 1) H₂O 2) C₃H₆O                               | 15+5                                    |
| 183, stand+H₂O₂    | KEF-0.2 (100), 25                                                       | 1)H₂O 2) H₂O₂ 3) C₃H₆O                       | 5+10+5                                  |
| 184, stand+HF      |                                                                         | 1)H₂O 2)HF:C₃H₆O 3)C₃H₆O                      | 5+10+5                                  |

Chemical bonds in porous silicon were analyzed with the use of a Vertex 70 infrared Fourier-spectrometer (Bruker) applying an attachment for attenuated total reflection spectroscopy.

3. Results and discussion
According to SEM data (JEOL JSM 6380LV), the investigated post-treatment processes did not result in noticeable changes in the morphology of the samples. SEM images of the cleavage and surface of the samples are presented in figure 1.

IR-transmission spectra for the samples of porous silicon are presented in figures 2-4. They were obtained 3 and 45 days after the preparation and post-treatment of the samples (functionalization). All this time, the samples were stored in laboratory conditions in closed plastic bags.

According to the IR-spectroscopy data, after 3 days of storage in the atmosphere in the spectrum of a “standard” sample one can observe the spectral bands characteristic of porous silicon, attributed to Si–Si and Si–H bonds (616 and 634 cm⁻¹) and the band at 750-1000 cm⁻¹, corresponding to various kinds of Si–H and O₃Si₅ bonds (see figure 3). One can also see the oxide composite peak Si-O-Si (1060-1250 cm⁻¹) and the band at 2150-2250 cm⁻¹, corresponding to different kinds of vibrations
attributed to the bonds of adsorbed hydrogen and oxygen-containing groups (2084 cm$^{-1}$ Si-H stretching longitudinal, 2110 cm$^{-1}$ Si-H$_2$ stretching longitudinal, 2200 cm$^{-1}$, SiH-SiO$_2$ structural vibrations, 2245 cm$^{-1}$ O,SiH valence vibrations) [8].

![SEM images](image1)

**Figure 1.** SEM images of a) cleavage and b) surface of mesoporous silicon obtained according to the “standard” technique (sample Standard, an analogue of sample N3)

![IR spectra](image2)

**Figure 2.** IR-transmission spectra of porous silicon samples (three days after their obtaining) with different kinds of post-treatment.

Post-treatment of the samples in water and hydrogen peroxide resulted in additional oxidation of the samples compared to the standard technique of sample preparation. This is observed as an increase in the intensity of the absorption band corresponding to Si-O-Si bonds, compared with that attributed to Si-Si bonds. Moreover, post-treatment of the samples in water and hydrogen peroxide, as expected,
resulted in a decrease in the percentage of Si-Hx bonds on the surface of pores and a corresponding increase in the number of oxygen-containing O_xSiH_y bonds. The treatment in hydrogen peroxide undoubtedly resulted in stronger oxidation of the porous layer. Post-treatment in a fluoric acid solution, on the contrary, diminished the amount of oxide on the surface. This decrease was accompanied by an increase in the intensity of the bands corresponding to different types of Si-H bonds (figure 3).

![Figure 3. IR-transmission spectra of porous silicon samples with different kinds of post-treatment (3 days after obtaining the samples)](image)

After 1.5 months of exposure to laboratory conditions, a general tendency to oxidation was observed both for the standard sample and for the samples after post-treatment procedures (figure 4). It is manifested as a decrease in the intensity for the absorption band attributed to Si-Si and Si-H bonds (600-650 cm\(^{-1}\)) and an increase in the intensity for the band corresponding to Si-O- Si bonds (1000 - 1300 cm\(^{-1}\)). Moreover, for all the samples during their natural ageing, a decrease in the number of various Si-Hx bonds and an increase in the number of oxygen-silicon bonds of the O_xSiH_y type were found.

It can be observed as a considerable change in the shape of the absorption bands in the spectral ranges of 750-1000 cm\(^{-1}\) and 2050-2300 cm\(^{-1}\). It should be noted that the shape of the spectrum for the
samples treated in hydrogen peroxide has changed less than those for other samples after 1.5 months of exposure to the atmosphere.

![IR-transmission spectra of porous silicon samples with different kinds of post-treatment (45 days after obtaining the samples).](image)

**Figure 4.** IR-transmission spectra of porous silicon samples with different kinds of post-treatment (45 days after obtaining the samples).

### 4. Conclusions
It is shown in the work that even by applying the simplest post-processing techniques for porous silicon, significant changes in the composition of its surface can be achieved. The results can be used to create techniques for the formation of targeted drug delivery systems. Nevertheless, one should take into account the fact that during the natural ageing of the samples, the effects of the studied treatments are significantly reduced.

### Acknowledgments
The study was funded by RFBR and the Voronezh State Government according to the research project N 19-42-363004.

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