Effects of «simplest» post-treatment techniques on the composition of porous silicon surface

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Abstract. The article is concerned with the investigation of techniques of post-treatment of porous silicon. It was shown that the applied techniques have considerable effect on por-Si nanowires shell without a considerable influencing on their core. To study the features of changing the phase composition and the composition of chemical bonds of the surface of porous silicon, we used infrared spectroscopy, Ultrasoft X-Ray Spectroscopy and photoluminescence spectroscopy.

1. Introduction
Complicated 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 disadvantage of this material [1,2]. On the one hand, a wide set of possible morphology and composition characteristics opens up great possibilities for utilization of porous silicon in a lot of applicable problems, but on the other hand, it provides problems in a choice of the suitable technique for a certain practical application. In addition, this puts on limitations for its storage conditions and the following technological operations with this material [2].

For example, now a number of works are actively performed in the field of materials design in order to obtain a targeted delivery of medications where researchers try to introduce porous silicon nanoparticles into the living organisms or separate cells. It is important to note that the cells and organs do not experience toxic effect of silicon particles [3-8]. The surface of these particles can be inoculated with the molecules named bio-markers which are used in the diagnostics of the analyzed cells, as well as the medications applied for the recovery of the faulted cell functions. However, a high surface activity of porous silicon that allows adsorption of certain active molecules to its surface at the same time stipulates instability of the surface properties for this material[3-8].

Therefore, an important task in the work with porous silicon and nanopowders on the basis of this material is the controllable stabilization and further functionalization of its surface. So, in order to solve these problems several techniques were proposed: thermal annealing of porous silicon in the oxygen medium, carbonization, treatment in certain acids. However, these techniques are not applicable in the cases when the results of post-treatment lead to the formation of the phases that are not characteristic for the source material or to the appearance of the new morphological features or
either to the adsorbed products of reactions on their surface. For example, surface treatment under increased temperature is known to result in the appearance of additional mechanical stresses in the porous layer and to its cracking. In its turn, this can result in the degradation of the quality for the films grown on the structure at the further technological operations or in a decrease of the size of the synthesized nanoparticles [2,9-12]. This work is intended to demonstrate that even the simplest post-treatments can provide a significant impact on the composition of porous silicon surface and it luminescence characteristics.

2. Materials and methods
Porous silicon samples were obtained by electrochemical etching of single-crystalline silicon of KEF (P-doped) (100) type with a resistivity of 0.2 Ohm*cm. Solution on the basis of 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. Standard post-treatment of the samples applied for removal of the reaction products and a partial passivation of the surface included rinsing in the distilled water and soaking in isopropyl alcohol for 5 minutes in both procedures.

Below, 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 for producing of porous silicon. Technique for post-treatment of the surface was chosen on the basis of the general ideas concerning the etching mechanism while obtaining of the porous silicon.

Thus, trying to perform additional oxidation of porous silicon surface according to the reaction \( \text{Si} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{H}^+ \) additional treatments were implemented by soaking in the distilled water and 30% solution of hydrogen peroxide, while in order to decrease the fraction of surface oxides according to the reaction of \( \text{SiO}_2 + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O} \), chemical sub-etching in the alcoholic solution of fluoric acid was selected as HF:C\(_3\)H\(_7\)OH 1:5. Technique of production and the steps of post-treatment are presented in details in Table 1.

| Series, designation | Type of the plate of single-crystalline silicon, current density, mA/cm\(^2\) | Post-treatment, order of the process, solution | Time of post-treatment over the steps, min. |
|---------------------|-------------------------------------------|---------------------------------------------|------------------------------------------|
| stand.              | KEF-0.2 (100), 25                         | 1)\(\text{H}_2\text{O}\) 2)\(\text{C}_3\text{H}_8\text{O}\) | 5+5                                      |
| stand. +\(\text{H}_2\text{O}\) |                                           | 1) \(\text{H}_2\text{O}\) 2) \(\text{C}_3\text{H}_8\text{O}\) | 15+5                                     |
| stand. +\(\text{H}_2\text{O}_2\) |                                           | 1)\(\text{H}_2\text{O}\) 2)\(\text{H}_2\text{O}_2\) | 5+10+5                                   |
| stand. +HF          |                                           | 3) \(\text{C}_3\text{H}_8\text{O}\)         | 5+10+5                                   |

To study the influence of post-treatments on the composition of porous silicon the following analytical techniques were applied: IR, photoluminescence (PL) spectroscopy as well as ultrasoft X-ray emission spectroscopy (USXES). Chemical bonds in porous silicon were analyzed with the use of infrared Fourier-spectrometer Vertex 70 (Bruker) applying an attachment for attenuated total reflection spectroscopy. Using X-ray spectrometer-monochromator RSM-500 by USXES technique phase composition of the samples in the near-surface area of the samples was studied (depth of analysis was of 60 nm). Luminescence spectra were registered with fiber-optics spectrometer USB4000-VIS-NIR (Ocean Optics), connected to the computer. Laser diode radiating at the wavelength of 405 nm was utilized as a source of excitation.
3. Results and discussion
According to SEM data the investigated post-treatment processes did not result in the noticeable changes in morphology of the samples. SEM images of the cleavage plane and surface of the samples are presented in figure 1.

Figure 1. SEM images of: a) cleavage plane and b) surface of mesoporous silicon obtained according to the “standard” technique (sample Standard, analogue of the sample №3).

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

Figure 2. IR-transmission spectra of the porous silicon samples (three days after their obtaining) with different kinds of post-treatment.
According to the IR-spectroscopy data after 3 days of storage in the atmosphere in the spectrum of "standard" sample spectral bands can be observed characteristic for porous silicon, attributed to Si–Si and Si–H bonds (616 and 634 cm\(^{-1}\)), the band at 750-1000 cm\(^{-1}\), corresponding to various kinds of Si–H and O\(_x\)Si\(_y\) bonds (see figure 3); one can also see 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\(_2\)SiH valence vibrations) [13].

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

1.5 months later under exposure in the laboratory conditions a common tendency to oxidation was observed as for the standard sample, as for the samples after post-treatment procedures (figure 4). It is manifested as a decrease of intensity for the absorption band attributed to Si-Si and Si-H bonds (600-650 cm\(^{-1}\)) and increase of intensity for the band corresponding to Si-O-Si bonds (1000 -1300 cm\(^{-1}\)). Moreover, for all of the samples during their natural ageing a decrease of different variants of Si-H\(_x\) bonds and increase of the number of oxygen-silicon bonds of O\(_x\)SiH\(_y\) type can be seen. It is observed as a considerable change in the shape of absorption bands in the spectral intervals 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 changed less than those ones for other samples after 1.5 months of exposure in the atmosphere.

Electron structure of the valence band in porous semiconductors was studied using ultrasoft X-ray emission spectroscopy (USXES) technique. It enables to obtain information on the occupied electron states in the materials with rather high energy resolution.

In order to simulate phase composition of the investigated porous silicon samples X-ray emission spectra were represented as a sum of Si L\(_{2,3}\) spectra of the reference phases involving silicon: single-crystalline silicon c-Si, amorphous hydrogenated silicon a-Si (a-Si:H), and two kinds of silicon oxides – silicon sub-oxide SiO\(_{1.3}\) and silicon dioxide SiO\(_2\). All of the spectra for the reference substances were retrieved from our previous work [13]. X-ray spectra of the investigated structures were obtained 3.5 months after preparation of the samples and their post treatment under accelerating voltages at the X-ray tube anode of 3 kV that provided the depth of analysis of about 60 nm. The data obtained in these experiments are presented in Table 2 and in the figure 5.

![Figure 5. USXES Si L\(_{2,3}\) spectra of porous silicon samples with different kinds of post-treatment (3.5 months after obtaining of the samples). Black line – experiment, red line – fitting according to [14,15].](image)

**Table 2.** Distribution of the components in the phase composition as their percentage in the porous silicon samples with different kinds of post-treatment (functionalization).

| Sample          | c-Si, % | a-Si:H, % | SiO\(_{1.3}\), % | SiO\(_2\), % | Error, % |
|-----------------|---------|-----------|-----------------|-------------|----------|
| stand.          | 37      | 32        | 9               | 22          | 9        |
| stand. +H\(_2\)O| 37      | 11        | 18              | 34          | 8        |
| stand.+H\(_2\)\(_2\)O\(_2\)| 30    | 20        | 0               | 50          | 8        |
| stand.+HF       | 32      | 45        | 0               | 23          | 10       |

USXES results are in good agreement with IR spectroscopy data. Basing on the problem definition including the change of surface layer composition utilizing post-treatment procedures, namely, to attain an additional oxidation or, on the contrary, to remove a part of oxide layer from the surface of porous layer, after analysis of the USXES data (depth of analysis is about 60 nm) one can conclude the following. Soaking of the samples in the distilled water and in the solution of hydrogen peroxide
results in the change of the ratio of the oxidized (SiOx + SiO2) and non-oxidized phases (c-Si + a-Si:H) in the porous layer from ~ 30%:70 % to 50%:50%. Note, that the treatment of the sample in hydrogen peroxide leads to the formation of the phase of silicon oxide with a greater degree of oxidation (SiO2) on the surface of silicon wires in por-Si. Treatment of por-Si surface in the solution of fluoric acid, on the contrary, leads to a decrease of oxides contribution into composition of the porous layer up to ~ 20:80, as a result of the dissolution of defect silicon oxide with the formation of a-Si:H. It should be specially noted that the use of post-treatments in our investigations does not in fact change (with the account of errors of simulation) the percentage of crystalline silicon within the porous layer of the samples. Basing on the quite well-established ideas on the phase composition of por-Si, where the fragments (wires, columns, arrays of nanoparticles) are distinguished by the presence of crystalline core inside, covered by the layer of amorphous silicon with a gradual transfer to sub-oxide and dioxide of silicon in the ratios depending on the technique of production. Applying the presented post-treatment procedures, we can control the composition of the core “shell” of the nanostructures without a noticeable effect on the “core”. This result can be of a great importance for different practical applications of porous silicon. This behavior was also observed in the porous layer for the greater depth of analysis (120 nm). In all of the samples the contribution of non-oxidized phases into the phase composition was expected to be enhanced with depth of analysis [14].

Photoluminescence spectra (PL) of the porous silicon samples were measured with the use of fiber-optical spectrometer USB4000-VIS-NIR (350-1000 nm) produced by OceanOptics company. Photoluminescence spectra excited by the radiation with λ = 405 nm are presented in figure 7 were obtained 1.5 months later after preparation of the samples.

![Figure 6. Photoluminescence spectra of porous silicon samples before and after post-treatment.](image)

According to PL data the utilized post-treatments resulted in a decrease of intensity of the photoluminescence band in the primary porous silicon samples while its position and bandwidth is kept invariable. In addition, basing on the conventional ideas concerning phase composition of porous silicon and quantum-size model of its PL it is also possible to make a conclusion that the applied experimental techniques have no serious effect on the mean size of silicon nanocrystallites forming the “core”, responsible for the bandwidth and position of PL peak. However, they have a significant impact on the “shell” consisting of amorphous and oxide phases. An increase of the “shell” contribution to the phase composition of the investigated silicon nanostructures, presented in the form of amorphous (hydrogenated) silicon and in the form of silicon sub-oxides and dioxide, leads to a considerable decrease of PL intensity. This result is in a good agreement with the ideas on the negative impact of the defects in silicon sub-oxide and hydrogen bonds on PL properties of por-Si, resulting in
the formation of a great number of non-radiative recombination centers. Thus, one can conclude that in order to improve PL properties of porous silicon in the visible and near-IR spectral range it is necessary to form silicon nanostructures consisting mainly of the (nano)crystalline core with a thin shell of the perfect oxide SiO$_2$.

4. Conclusions
Freshly obtained porous silicon demonstrates instability of the chemical composition: surface of the pores is covered with hydrogen weakly bound to silicon atoms. At the same time Si-OH complexes are also formed in the while etching of crystalline silicon. Later on weakly bound hydrogen starts to release from the pores while the dangling unstable bonds of silicon are passivated by the atmospheric oxygen. The interaction of the surface silicon atoms with water vapour from the atmosphere is also a common reaction when keeping of por-Si samples in the atmosphere. The processes occurring in porous silicon layer is considered as ageing. Ageing of por-Si is difficult to control and regulate. That is why post-treatment procedures are highly recommended after producing of porous silicon.

It was found that even simplest post-treatment techniques can significantly change the chemical composition of silicon nanowire shell. Increase of silicon oxide and amorphous phase content in the por-Si nanowire shell results in degradation of its PL intensity.

5. References
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