The effect of anodization current density on the functionalization of porous silicon nanoparticles with an antibiotic

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Abstract. The influence of the anodization current density to the morphology and composition of the surface of porous silicon before and after its impregnation with an antibiotic was investigated using atomic force microscopy and IR spectroscopy. Layers of porous silicon were obtained by electrochemical etching; variable technological parameters of anodizing were the current density and the type of conductivity of the silicon plate. The results obtained are discussed in terms of their use in targeted drug delivery.

1. Introduction

Nanoparticles of porous silicon (por-Si) are extremely relevant for use in medicine, in particular for targeted drug delivery as porous transport carriers, in theranostics, etc. [1-5]. A unique combination of such properties of por-Si as biocompatibility, biodegradability, multi-functionality (not only as a carrier matrix, but also the sensor, marker, etc. due to the ability to photoluminescence in the spectral range of organisms transparency), the ability to easily tune the properties of a porous particle (porosity, surface development, hydrophobicity, surface charge state, local charge distribution, etc.) in wide ranges with the relative simplicity of the production technology provides its competitive advantages compared to other carrier materials for targeted drug delivery [3, 4].

It is known that the morphology and phase composition of the n-type por-Si surface may noticeably differ depending on the choice of technological conditions of electrochemical treatment [7, 9]. At the same time, hydrophilic and hydrophobic, acid-base and donor-acceptor properties of the material surface, determined by the presence of certain centers and functional groups on it, significantly affect such characteristics of the material as: wettability, the nature of the permeability of organic molecules with different chemical compositions into pores, the interaction of por-Si with physiological fluids and drugs [3, 5, 9]. Thus, by controlling the technological parameters for obtaining por-Si it is possible to set the morphology and composition of the surface that are most effective for the adsorption of a particular drug or filler (various molecular sizes, hydrophilic or hydrophobic molecules, etc.).

The paper discusses the features of the effect of anodizing current density on the morphology and surface composition of nanolayers por-Si with different types of conductivity before and after functionalization with Kanamycin (Kan) antibiotic.
2. Material and method
Nanolayers of por-Si were obtained by electrochemical anodic etching. The choice of process conditions (initial material: phosphorus doped n-type silicon <111> wafer with a resistivity 4.5 Ω·cm, anodization current density: je = 30 mA/cm² and j = 80 mA / cm², anodization time of t = 10 min) was based on the experience of previous studies [3, 6]. As another initial material, a p-type silicon <111> wafer doped with boron with a resistance of 10 Ω·cm was chosen, since porous nanolayers obtained from this material haven’t yet been studied as n-type por-Si nanolayers. Pre-processing of the samples and post-processing after electrochemical etching, were carried out for all samples in the same way. Electrochemical anodizing of silicon was carried out in an electrolyte based on an aqueous-alcohol solution of hydrogen fluoride.

For functionalization such prepared nanolayers impregnation method was chosen. The nanolayers were immersed into saturated drug solution of antibiotic Kanamycin sulfate for 24 hour. The medicine substance Kanamycin sulfate was chosen because it is a broad-spectrum antibiotic, often used to treat socially significant diseases as a tuberculosis. The Kanamycin sulfate molecules contain amino and hydroxyl groups. Therefore, porous silicon was obtained in such technological conditions for hydrophilic por-Si surface. This contributes to a more successful binding of medicine molecules to a porous particle; we believe that their interaction occurs through oxygen bridges.

The morphology of por-Si obtained under close conditions was studied by the Atomic force microscopy (AFM) method in the contact mode by means of Ntegra TERMA probe nanolaboratory (NT-MDT, Zelenograd). CSG01 AFM probes were chosen appropriate to the contact mode study. Since it was known from previous studies in our laboratory that porous silicon with several types of pores is formed under the selected conditions [3], the surface was recorded in the AFM at different scanning scales. To verify the reproducibility of the AFM data, morphology studies were carried out on several samples of each type, at least 3 points on the surface of the sample were selected, several AFM probes CSG01.

The composition of functional groups on the surface of porous silicon before and after functionalization was studied by reflective IR spectroscopy. Reflection spectra were acquired using an IR-Fourier spectrometric complex based on the Nicolet-6700 instrument. As a comparison sample was used Gold (test sample).

3. Results and discussion
Figure 1 and 2 shows the surface morphology of the obtained samples. It can be noted that the surface of the samples is uniform, mesopores of about 45-55 nm in diameter for n-por-Si and 50-60 nm for p-por-Si are observed. The pore density for these samples was also comparable in values: 12.5x10⁸ cm⁻² for n-por-Si and 14x10⁸ cm⁻² for p-por-Si, which exceeds the dislocation density in the initial silicon wafers and is most likely determined to a greater extent by the composition of the electrolyte for electrochemical etching (mole fraction of HF²⁻ ions), as well as the current density of the anodizing.

![Figure 1](image_url)

**Figure 1.** The surface morphology of the p-por-Si (111) obtained for j=20 mA/cm², t=10 min. at two scanning field scales: (a) 5 µm x 5 µm and (b) 1 µm x 1 µm, respectively.
Figure 2. The surface morphology of the n-por-Si (111) obtained for j=20 mA/cm², t=10 min. at two scanning field scales: (a) 5 µm x 5 µm and (b) 1 µm x 1 µm, respectively.

Some differences between n-and p-are observed. The morphology of the n-por-Si surface is smoother, in contrast to it, the p-por-Si surface has a quasi-ordered structuring of the surface: smooth macro-depressions with a diameter of about 800 nm are formed (figure 2, a). The density of such pores does not change during the studied period of anodizing (0,32x10⁸ cm⁻²).

All the obtained samples of porous silicon before and after kanamycin functionalization were studied by the method of reflective IR spectroscopy. IR spectra of por-Si layers at a given current density of anodizing are shown in figure 3 and 4. The observed reflection bands are interpreted in accordance with reference data [4, 7, 10] and summarized in table 1.

Table 1. IR absorption peaks in the por-Si samples interpreted according to [4, 7, 10].

| No* | Bandposition, (cm⁻¹) | Interpretation | n-por-Si | n-por-Si<Kan> | p-por-Si | p-por-Si<Kan> |
|-----|----------------------|----------------|---------|-------------|---------|-------------|
| 1   | 3610                 | vibration OH⁻ in SiOH | +       | -           | +       | +           |
| 2   | 3452                 | vibration OH⁻ in H₂O | +       | +           | -       | +           |
| 3   | 2958                 | Antisymmetric stretching vibrations CH⁻ in CH₃ | +       | +           | -       | -           |
| 4   | 2927                 | Antisymmetric stretching vibrations CH⁻ in CH₂ | +       | +           | +       | +           |
| 5   | 2858                 | Antisymmetric stretching vibrations CH⁻ in CH | +       | +           | +       | +           |
| 6   | 2248                 | vibration SiH⁻ in O₂-SiH | +       | -           | -       | -           |
| 7   | 2087                 | vibration SiH⁻ in Si₂H-SiH | -       | -           | +       | -           |
| 8   | 1463                 | CH₃⁻, antisymmetric deformation vibrations | +       | +           | -       | +           |
| 9   | 1230                 | Symmetrical deformation SiCH₃ | +       | +           | +       | -           |
| 10  | 1160-1056            | stretching antisymmetric vibrations SiO⁻ in O-SiO | -       | -           | +       | +           |
| 11  | 948                  | SiH⁻ in Si₂H-SiH | -       | +           | +       | -           |
| 12  | 906                  | SiH₂⁻ scissor vibrations | +       | +           | -       | -           |
| 13  | 827                  | stretching symmetric vibrations SiO in O-Si-O | +       | +           | +       | -           |

A comparative analysis of the IR spectra of pure n-type porous-Si layers in figure 3 and 4 showed that for almost all samples, a wide absorption band corresponding to surface hydroxyl groups (O – H
bonds) is observed in the region of 3000–3800 cm$^{-1}$. The reason for this is the technological conditions of the post-processing of porous-Si for achieving hydrophilic surface.

The porous-Si spectra over the entire current density range contain typical absorption bands at 2958 cm$^{-1}$, 2927 cm$^{-1}$, and 2856 cm$^{-1}$, indicating the presence of organic compounds (carbon-containing complexes) on the surface of porous-Si. Moreover, the intensity is higher for samples obtained at a higher anodizing current density. The appearance of organic compounds (carbon-containing compounds) on the porous-Si surface is associated with the electrochemical oxidation of alcohol, which is part of the electrolyte, on the porous-Si surface, which leads to the appearance of C = O groups that can interact with hydroxyl groups. Passivation of the surface with hydrogen, typical of porous-Si anodized in an aqueous electrolyte, is also observed.

**Figure 3.** IR spectra of porous silicon nanolayers obtained at J=30 mA/cm$^2$ before and after functionalization

**Figure 4.** IR spectra of porous silicon nanolayers obtained at J=80 mA/cm$^2$ before and after functionalization
In the spectrum of 30n-porous-Si, a reflection minimum of 2248 cm\(^{-1}\) appears, associated with the vibrations of SiH\(_2\) in O-SiH. Also can be observed absorption lines at 1247 cm\(^{-1}\) and 906 cm\(^{-1}\) which are attributed to symmetrical deformation vibrations of SiCH\(_3\) and scissor vibrations of SiH\(_2\).

In the spectrum of 80n-porous-Si but there are absorption lines at 1456 cm\(^{-1}\), 956 cm\(^{-1}\) and 811 cm\(^{-1}\) related to antisymmetric deformation vibrations of CH\(_3\), SiH bond vibrations and valence symmetric vibrations of SiO.

Thus, for n-porous-Si formed from an n-type silicon substrate, with increasing current density anodizing is observed:

- hydrophilic character of the surface (presence of OH groups) is observed in a wide range of current density
- when the current density increases from 30 mA/cm\(^2\) to 80 mA/cm\(^2\), the typical surface composition is preserved (H passivation, Si oxidation with oxygen, the presence of CH\(_3\), CH\(_2\)-groups). Their ratio does not change much either: as the current density increases, the number of SiH bonds decreases slightly, and surface oxidation (Si-O) increases, which is consistent with current data in this area on more intensive surface oxidation at a higher current density (changing the ratio of parallel and sequential electrochemical processes).

The 30p-porous-Si spectrum shows the formation of organic compounds on the surface, which is confirmed on the spectrum by absorption lines at 2917 cm\(^{-1}\) and 2873 cm\(^{-1}\), which correspond to vibrations of CH bonds. Minima at 1733 cm\(^{-1}\) and 819 cm\(^{-1}\) are also observed, which correspond to CO vibrations and symmetric stretching vibrations of SiO in O-Si-O.

The spectrum of 80p-porous-Si, in comparison with the spectra analysed above, is partially different in that new absorption lines are observed on it. For example: SiH vibrations are observed in Si\(_2\)-H-SiH and in Si\(_2\)-H-SiH at 2058 cm\(^{-1}\) and 958 cm\(^{-1}\), stretching antisymmetric SiO\(^-\) vibrations in O-SiO and in CSiO at 1066 cm\(^{-1}\) and 1182 cm\(^{-1}\). Also can be noticed that the absorption line at 1259 cm\(^{-1}\) associated with the deformation symmetric SiCH\(_3\).

Analysing these spectra, it can said that as the current density increases, the surface composition changes. This is confirmed by the appearance of different reflection minima corresponding to different vibrations of different molecules formed on the surface.

Thus, for n-porous-Si and p-porous-Si there are general patterns:

- Si-Si, Si-O, Si-H, CH\(_3\) -, CH\(_2\)-bonds are formed on the surface and their ratio changes depending on the current density;
- all spectra contain absorption bands associated with –OH group, but on the surface of n-porous-Si there are significantly more of them;
- but in the spectra of p-porous-Si, there is less oxygen and more carbon pollution;

In the spectra of 30n-porous-Si-Kan, compared with pure n-porous-Si at the corresponding anodizing current densities, no significant differences were observed. Comparing the spectra of 80n-porous-Si and 80n-porous-Si-Kan, can be said that the low intensity of the minimum reflects the presence on the surface. In this case, the absorption is increased by 1200 cm\(^{-1}\) and 1160 cm\(^{-1}\). This increases the binding capacity with porous Kanamycin molecules.

Analysing the spectra of p-porous-Si before and after functionalization, we can say that in general, there are no significant changes in the surface composition. The only difference between the p-porous-Kan spectra is that absorption bands associated with hydroxy groups appear.

4. Conclusion

Analysing the IR-spectra for n- and p-porous-Si revealed the following features. For n-porous-Si a more hydrophilic surface is observed - in the IR reflection spectrum there is a wide absorption band (≈ 3100-3600 cm\(^{-1}\)), in contrast to p-porous-Si obtained under the same technological conditions of anodization. Absorption bands are present on the surface of all samples due to the presence of Si – H and Si – O bonds and the presence of CH– groups in CH\(_3\) and CH– in CH\(_2\), in different ratios depending on the conditions of preparation. On the p-type surfaces form more organic compounds. It was shown that the IR spectra with increasing anodization current density on the n-porous-Si surface slightly decrease the number of Si-H bonds and increase the presence of oxidized silicon atoms.
It was observed no significant changes in the surface composition of p-porous-Si before and after functionalization by Kanamycin on IR spectra. The only difference between the spectra of p-porous-Si-Kan is that there is an absorption band associated with hydroxyl groups. Studies of porous silicon samples after impregnation of Kanamycin sulphate demonstrated the most significant changes for porous silicon obtained at 80 mA/cm$^2$. A comparison of the IR spectra of 80n-porous-Si and 80n-porous-Si-Kan showed an increase in the absorption at 1200 cm$^{-1}$ and 1160 cm$^{-1}$. This changes are associated with the replacement of Si-H$_x$ bonds on the surface of porous-Si by Kanamycin molecules. At the same time, the intensity of the reflection minimum associated with the presence of Si-H$_x$ bonds on the surface also decreases. Thus, from the conditions studied, this type of porous silicon is most effective for creating porous carriers based on it for targeted delivery of this type of antibiotic.

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