Porous silicon for drug delivery systems

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Abstract: The article deals with main principles of the formation of porous silicon (por-Si) to produce containers for drug delivery systems. Most important por-Si characteristics to produce nanocontainers with required parameters are determined.

1. Introduction
Using nanostructured containers for directional drug delivery is one of the fast developing trends in the medical field. Firstly, it is connected with the low effectiveness of traditional ways of introducing drugs and consequent negative effects. So, the development of undangerous container’s materials for the aims mentioned above is one of the most important tasks for medicine and material science. Porous silicon (por-Si) is extremely promising material for such containers. In the first turn it is stipulated by its bio-compatibility, bioaccessibility, biodegradation and nontoxicity. Despite being complicated, electrochemical processes of por-Si formation are rather technically simple to carry out and inexpensive [1].

Main characteristics of the material for its use as containers are the radial and axial pore dimensions, pore partition width, porosity, surface extension measure. These parameters depend on the silicon wafer properties (the conductivity type, dopant concentration, structure imperfections, etc.) as well as the porous etching conditions (electrolyte solutions composition, current density, etching time, etc.).

To take into consideration all the factors mentioned above, which are very important to obtain por-Si with previously assigned parameters, is extremely difficult and likely unachievable.

That’s why in our opinion to get por-Si with required parameters it is more reasonable to determine the general principles of por-Si formation and how porous layers parameters are dependent on them. Such an approach will let choose specific etching conditions to obtain materials with characteristics, matched the needed extents.

Solution for the problems is the main aim of the research.

2. Experimental
We used n- and p-type silicon wafers with the resistivity in the range $\rho = 0.01 – 100$ ohm·cm, oriented long the (100) and (111) crystallographic planes. The wafers were etched with hydrofluoric acid solutions (45% HF) in H$_2$O in the volume ratio 2:1 in a galvanostatic mode. The etching cell, made of Teflon, allowed for one-sided horizontal etching. The anode used was a polished massive copper plate,
and the cathode had the form of a thin platinum plate. The electric field applied during etching was varied by diaphragms of various sizes and changing the electrode separation.

The nanopore size, shape, and orientation and thickness of NS layers were determined using a JEOL electron microscope and a POLARM R optical microscope.

3. Experimental results and discussion
Historically the formation of por-Si was considered as interaction between silicon and F ion in HF solutions [1-4]. The correlation between the etching process parameters and the parameters of por-Si was explained on the basis of this approach.

We have revealed [5-7] that porous etching of Si is stipulated not F ion, but (HF$_2$)$^-$ ion, which is contained in HF solutions > 1mol/l.

Difference between the two ions, including their sizes, structures, anisotropy, causes inequality in the interaction of Si with F and Si with (HF$_2$)$^-$, what was described in our articles [4]. Thus, it influences the pore formation in Si with various parameters.

To produce containers of por-Si with required parameters one should process silicon wafer to get porous material with appropriate characteristics. From this point of view, the most important por-Si ones are radial and axial pore dimensions, pore partition width, porosity, surface extension measure. Therefore, this article focuses on general regularities determining the characteristics mentioned above.

On the first figure (figure 1) there is the influence of etching time (t) on the thickness of porous layers obtained on n- and p-type silicon wafers with various dopant concentration under various current density (j). The figure 1 shows, that under processing conditions being equal, the thickness of n-type porous layers significantly outstrips the thickness of p-type porous layers. The thickness of por-Si layers, obtained on silicon wafers with P dopant (n-type) 8·10$^{14}$ cm$^{-3}$ ($\rho$= 5 ohm·cm), 4·10$^{14}$ cm$^{-3}$ ($\rho$= 10 ohm·cm), j=25 mA/cm$^2$, t=30 minutes, was 180-220 micron. The thickness of por-Si layers, obtained on silicon wafers with B dopant (p-type) 1.2·10$^{15}$ cm$^{-3}$ ($\rho$= 10 ohm·cm) with other conditions being equal, did not exceed 50-60 micron. Current density from 1 mA/cm$^2$ to 50 mA/cm$^2$ does not result in essential thickness changes under the same etching time.

![Figure 1](image.jpg)

**Figure 1.** The dependence of por-Si layers thickness on the etching time.

According to the results [8] pore axial dimension depends on two simultaneous processes: Si surface etching with F ions (some quality of which constantly exist in HF solutions of any concentration) and porous etching with (HF$_2$)$^-$ ions. It means that axial pore dimension is limited by the equilibrium between rates of the two processes. This fact should be taken into account to predict axial pore dimension (h) (equation 1).

The figure 2 shows the dependence between pore frequency function and electric-field intensity. The pore frequency function increases while the electric-field intensity decreases.
The dependence of pore frequency function on electric-field intensity: the distance between the cathode and the anode (a) 2.5 cm, (b) 7 cm

The influence of the dopant concentration on the pore frequency function can be esteemed on the figure 3, which shows how pore radial dimension depends on the dopant concentration.

Figure 3. The dependence of the pore radial dimension on Si wafer resistivity: (1) n-Si, (2) p-Si.

According to [8-9] parameters of por-Si more suitable for producing drug delivery systems are 5-25 nm pore radial dimensions and 50% porosity.

From figure3 one can see, that the near-linear correlation between pore radial dimensions (10-15 nm, p=0.01 ohm/cm; 600-700 nm, p=10 ohm/cm) and Si resistivity (p) are observed over the 0.01 to 10 ohm/cm range. The dopant type does not reveal any significant influence [2].

Pore partition widths in por-Si, obtained on wafers with $p>0.1$ ohm·cm, have the size near to the pore radial dimensions and much more than the pore radial dimensions for $p<0.1$ ohm·cm.

The quality of medical agent in por-Si includes the drug adsorbed in pores as well as on the surface of porous silicon. This fact is very important for medicines with high adsorbing capacity. From these point of view research results of the dependence of por-Si formation from silicon wafer crystallographic orientation is of great importance.

Therefore, investigations of the principles of pore orientation on the wafer are very important.

On the figure 4 there are the photos of por-Si layers, made on (100) and (111) wafers. Pores, generated on (100) wafers, are perpendicular to the substrate. As to pores on (111) wafers, the processes of their generation and growth are more complicated.
Firstly tetrahedral regions form. Then semi-squared pores grow from the tetrahedral region walls. So that, they are at some angle the substance surface. Such a mechanism of por-Si formation results in branched structures and large internal surface. It let these structures absorb more medicine.

While planning to make por-Si with necessary characteristics, it is beneficial to esteem the influence of the processing parameters. It can be done with equation (1):

\[ S = A \frac{m_1}{\rho h N} \]  

\( S \) – pore radial dimension, cm\(^2\); \( A \) – constant, stipulated the mechanism of Si and (HF\(_2\))\(^-\) interaction (we have calculated it to be 0.0625); \( m_1 \) – mass of Si removed during porous etching, g; \( \rho \) – the density of Si, g/cm\(^3\); \( h \) – porous layer thickness, cm; \( N \) – the number of pore initiation places per unit area. \( N \) depends on dopant concentration \( C \).

\[ N = f(C^2) \]  

4. Conclusions: main principles of por-Si formation are determined. It let choose one single silicon wafers and etching parameters to obtain por-Si with parameters required for drug delivery systems on its base and facilitate the choice.

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