Investigation of porous silicon obtained under different conditions by the contact angle method

A O Belorus, Y V Bukina, A I Pastukhov, D S Stebko, Yu M Spivak and V A Moshnikov

St. Petersburg State Electrotechnical University «LETI», Saint Petersburg, Russian Federation

stebel2015@yandex.ru

Abstract. This paper investigates a hydrophobicity/hydrophilicity of porous silicon by the contact angle method. Porous silicon series were obtained by electrochemical anodic etching of n-Si (100) and (111) under the current anodization density range of 5-120 mA/cm². For this purpose the original laboratory installation and the software «Measurement of contact angle» were developed. It is shown that, the contact angle can vary significantly (up to 80 degrees for (100)) depending on the current anodization Discussion of the results is carried out taking in account the composition of the functional groups and of surface morphology of the porous silicon. These results are important for developing porous silicon particles as nanocontainers in the targeted drug delivery.

1. Introduction

One of the modern trends in the development of medicine is targeted drug delivery. Porous materials are extremely important for this direction. The key characteristics of such materials are porosity, the type of porous texture, the morphology of the surface, the specified composition of specific functional groups on the surface, the hydrophilicity or hydrophobicity of the material [1-3]. Porous silicon (por-Si) is a promising material for use as nanocontainers for targeted drug delivery. One of the significant advantages of pore-Si is the possibility of obtaining this material in a wide range of porosity, pore diameters, surface composition, etc. by controlling the synthesis conditions.

For targeted drug delivery considerable attention must be paid to the nature of the adsorption of medicinal substances by the porous media. The character of the adsorption must obviously be different for a por-Si with different structure parameters and a functional composition of the surface. Also, the dose of the accumulated drug substance, the possibility of simultaneous functionalization by molecules of different sizes, the simultaneous attachment of hydrophilic and hydrophobic substances, and the like will depend greatly on the characteristics of the por-Si.

The study of such a complex heterophase porous brittle object as porous silicon requires a special approach to the choice of research methods. There are methods for determining the characteristics of porous silicon, which are important for its use in targeted drug delivery [4-6]. In addition to determining the geometric parameters of the porous texture, it is important to study the phase composition of the por-Si surface, its energy characteristics and the character of the adsorption centers on it [1, 3, 7, 8].
The indicator method provides a qualitative determination of the functional groups on the surface of insoluble solids [9, 10, 1]. This method is extremely sensitive and allows differing between functional groups of the same chemical composition, differing only in the electron density distribution. The detection of the surface functional groups of por-Si, prepared at certain conditions, needs much different kind of samples. It is advisable to investigate functional groups not over the entire range of pKa (negative decimal logarithm of the acid dissociation constant), but only at determined values. The presence of certain surface functional groups has a significant influence to possibility of functionalization of the por-Si surface by biomarkers. Kind of adsorption centers on the surface of material (acidic, basic or almost neutral hydroxyls centers) is directly connected with the level of hydrophilic or hydrophobic properties. Thus, after the determination of the level, it is possible to choose the most appropriate range of pKa for research by using method of contact angle. It allows to reduce number of samples that expedites the measurement process.

Thus, this article is devoted to the study of the energy characteristics of porous silicon, depending on the technological conditions of synthesis.

2. Experimental
Por-Si samples were obtained in the single-chamber electrochemical cell in an aqueous solution of HF and isopropanol mixture. The technological conditions of electrochemical anodization process are shown in table 1. The variable parameter was the anodization current density. It is expected that porosity, surface development, pore diameter will increase with increasing anodization current density, and the composition of functional groups on the PS surface will change (the portion of hydroxyl groups decreases, and the fraction of disordered silicon atoms increases) [1]. As a raw material, the single crystal n-Si (111) and (100) with a resistivity of 4.5 Ω·cm was used.

| Series | Si parameters | Si specific resistivity, Ω·cm | Anodizing time, min | Current destiny J, mA/cm² |
|--------|---------------|-----------------------------|---------------------|--------------------------|
| I      | n-Si (100), n-Si (111) | 4.5                         | 10                  | 5                        |
| II     |               |                             |                     | 15                       |
| III    |               |                             |                     | 30                       |
| IV     |               |                             |                     | 50                       |
| V      |               |                             |                     | 80                       |
| VI     |               |                             |                     | 120                      |

Further, the samples were investigated by the contact angle method (the static sessile drop method). We used a homemade laboratory installation. The scheme of the installation is shown on Figure 1. It includes data processing device 1; digital microscope 2 with horizontal optical axis, which is at the same plane with the sample of por-Si; switch image button 3, which is also turn on/off the backlight; mount system of digital microscope 4; the lever 5 to provide changing the focal length of microscope; optical axis 6 of microscope; drop 7; substrate 8 (polymer film that planted on the glass); adjustable table 9; movable mechanism 10. The drop of water was dripped to the layers of por-Si by means of mechanical feeder; then the drop was captured by digital microscope.

To calculate the contact angles (θ), the special program «Measurement of contact angle» was written in the visual programming language on LabView environment. The main feature of «Measurement of contact angle» is that program takes data from digital image of drop, which includes values of diameter and height, and calculates contact angle. Angle calculation accuracy is estimated at 1 – 5 degrees. This virtual instrument is fully automated and, in this way, it expedites the entire process of processing the data.
3. Results and discussion

The dependencies of the contact angle on the anodization current density are shown in Fig. 2. As one can see from Fig. 2, the dependence patterns for porous silicon of (111) and (100) differ significantly. A strong nonlinear character of the dependence with a minimum is observed for por-Si (100): the angle varies from 43° to 124°. The minimum corresponds to the current density of 30 mA/cm². At this anodization current density, the most hydrophilic por-Si properties in this series are obtained. At high and low current densities, porous silicon exhibits hydrophobic properties (contact angles are 108° and 121° relatively).

Figure 1. The scheme of the installation of the contact angle measuring

Figure 2. Contact angle, depending on the anodization current density for two types of crystallographic orientation of por-Si substrates
This kind of dependence, apparently, can be explained as follows. At low anodic current densities, the morphology of the por-Si surface, as a rule, is of the order of units of nanometers, which are orders of magnitude smaller in comparison with por-Si obtained at 20-30 mA/cm². Apparently, in this section of the dependence (1-30 mA/cm²), the predominant factor is the change in the composition and proportion of the functional groups on the por-Si surface during etching with different current densities. As the anodization current density increases, por-Si surface development, porosity and pore diameter increase, which leads to an increase in the contact angle of wetting.

The dependence θ = f(Jₐ) for por-Si (111) samples has an slowly increasing monotonic character and shows the hydrophobic properties of the surface. It can be assumed that in the formation of porous silicon in n-Si (111), the prevailing factor determining the hydrophobic character of the surface, in this case, is the morphology of the surface.

4. Summary
In this paper, porous silicon series were obtained at various anodization current densities in the range 5-120 mA/cm² in n-Si with crystallographic orientation of (111) and (100). By the method of the contact angle, it has been shown that as prepared n-por-Si (111) has hydrophobic properties that increase slightly as the anodization current density increases. This is apparently associated with an increase in the porosity and development of surface morphology. For n-por-Si (111), the dependence of the contact angle on the anodization current density is stronger, non-monotonic, characterized by a minimum at Jₐ = 30 mA/cm². We assume that this dependence is due to the predominant influence of the functional groups composition on the por-Si surface at low anodization current densities. At high anodization current densities, evidently, that increasing porosity and morphology roughness leads to increasing the contact angle.

Thus, by varying the conditions for obtaining porous silicon and the type of substrate, it is possible to control the wettability properties of the surface over a wide range of values. Also, the results of the work will allow us to select the more precisely the required range of technological conditions for further investigation of porous silicon by the indicator method.

This is important in the development of nanocontainers based on porous silicon in the targeted delivery of drugs. The obtained dependences will help to purposefully change the properties of por-Si surface for functionalization with medical substances, thereby controlling the character of the interaction of the specified substance with the porous matrix. Obtained information of the surface wettability of por-Si should improve the encapsulation efficiency of medical substances.

Acknowledgement
The work was supported by the Task of The Ministry of Education and Science RF № 3.6288.2017/8.9 BC (basic part).

References
[1] Spivak Yu M, Myakin S V, Moshnikov V A, Panov M F, Belorus A O and Bobkov A A 2016 Surface functionality features of porous silicon prepared and treated in different conditions J. of Nanomater. 2016 2629582
[2] Belorus A O, Bespalova K and Spivak Yu M 2016 Morphology and internal structure of porous silicon powders in dependence on the conditions of post-processing Proc. IEEE NW Russia Young Researchers in Electrical and Electronic Engineering Conf. (St. Petersburg) (St. Petersburg, Russia: Saint Petersburg Electrotechnical University “LETI”) p 22-27
[3] Koshevoi V L, Pscheloko N S, Belorus A O and Levitskiy V S 2016 The study of the phase composition of polymorphous silicon film by Raman spectroscopy Proc. IEEE NW Russia Young Researchers in Electrical and Electronic Engineering Conf. (St. Petersburg) (St. Petersburg, Russia: Saint Petersburg Electrotechnical University “LETI”) p 62-64
[4] Belorus A O, Maraeva E V, Spivak Yu M and Moshnikov V A 2015 The study of porous...
silicon powders by capillary condensation J. of Phys.: Conf. Series 586 12-17
[5] Spivak Yu M, Belorus A O, Somov P A, Tulenin S S, Bespalova K and Moshnikov V A 2015 Porous silicon nanoparticles for target drag delivery: structure and J. of Phys.: Conf. Series 643 012022
[6] Kovalevskii A A 1999 Structure and morphology of Si films grown on Porous Silicon by reduction of Dichlorosilane Inorganic materials 35 152-156
[7] Lenshin A S, Kashkarov V M, Spivak Yu M and Moshnikov V A 2012 Study of electronic structure and phase composition of porous silicon Glass Phys. and Chem. 38 315-321
[8] Lenshin A S, Kashkarov V M, Spivak Yu M and Moshnikov V A 2012 Investigations of nanoreactors on the basis of p-type porous silicon: electron structure and phase composition Materials Chem. and Phys. 135 293-297
[9] Vasiljeva I V, Mjakin S V, Rylova E V and Korsakov V G 2002 Electron beam modification of the surface of oxide materials (SiO$_2$ and BaTiO$_3$) Russian J. Phys. Chem. 76 71-76
[10] Mjakin S V, Sychov M M and Vasilieva I V 2006 Electronno-luchevoe modifitsirovanie funktsionalnykh materialov (Electron beam modification of functional materials) (Saint-Petersburg: Petersburg State Transport University)