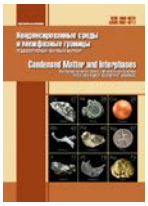

ISSN 1606-867X (Print)
ISSN 2687-0711 (Online)
Condensed Matter and Interphases
Kondensirovannye Sredy i Mezhfaznye Granitsy
https://journals.vsu.ru/kcmf/

Original articles

Research article
https://doi.org/10.17308/kcmf.2021.23/3535

An integral feature of porous silicon and its classification

A. M. Khort✉, A. G. Yakovenko, Yu. V. Syrov

MIREA – Russian Technological University. Institute of Physics and Technology,
78 Prospekt Vernadskogo, Moscow 119454, Russian Federation

Abstract

Porous silicon is currently one of the most studied materials which is used both in the areas traditional for silicon, such as electronics and optoelectronics, and in completely unconventional ones, such as catalysis, energetics, biology, and medicine. The multiple possibilities of the material are revealed due to the fact that its structure can be radically different depending on the properties of the initial silicon and the methods of obtaining porous phases. The use of any material inevitably leads to the need to classify its various forms. The purpose of the article was to find the most significant parameter that can be used as the basis for the classification of porous silicon.

Historically, the terminology defined by the IUPAC pore size classification has been used to classify porous silicon. Due to the authority of IUPAC, many researchers have considered this terminology to be the most successful and important, and the radial pore size has often been regarded as a main parameter containing the most important properties of porous silicon. Meanwhile, the unique properties and practical application of porous silicon are based on its developed inner surface. The method of nitrogen porosimetry, which is simple in its practical implementation, is often used in scientific literature to determine this value.

The most suitable integral parameter for the classification of porous silicon, regardless of its structure and morphology, is the total specific internal surface (cm^{-1}) that can be relatively easily established experimentally and is of fundamental importance for almost all applications of porous silicon. The use of this value does not exclude the use of other parameters for a more detailed classification.

Keywords: Porous silicon, Classification, Radial pore size, Nitrogen porosimetry, Ttotal specific internal surface area

For citation: Khort A. M., Yakovenko A. G., Syrov Yu. V. An integral feature of porous silicon and its classification. *Kondensirovannye sredy i mezhfaznye granitsy = Condensed Matter and Interphases.* 2021;23(3): 440–444. https://doi.org/10.17308/kcmf.2021.23/3535

Для цитирования: Хорт А. М., Яковенко А. Г., Сыров Ю. В. Интегральный признак и классификации пористого кремния. *Конденсированные среды и межфазные границы*. 2021;23(3): 440–444. https://doi.org/10.17308/kcmf.2021.23/3535

✉ Andrei M. Khort, e-mail: poristsil@yandex.ru

1. Introduction

There are a great number of publications related to the study of porous silicon (PS), which shows increased interest to this material. The range of practical application of PS is potentially wide, from electronics, optoelectronics, and lithium-ion batteries to medicine [1, 6]. In simplistic terms, the properties of the material itself are determined by such parameters of porous layers as radial and axial pore size, interporous distances, and related density of pore distribution.

Currently, the following parameters are used in scientific literature to characterise the PS layers of various functional purpose: porosity, luminescence radiation wavelength, radial pore size, and some others. Certainly, each of these parameters describes the material only from the point of view of its functional use. At the same time, porosity is often mentioned as an "integral" parameter of PS which is the determining one for the properties of this material. However, this parameter is not significant for porous silicon, unlike most porous materials. It only indicates the correlation between the volume of the etched silicon and the full volume of silicon subjected to etching and is not related to the main properties of the material. This parameter is more likely to be applied to macrosystems and it carries certain functional information for the description of density and partly for the description of specific thermal and electric conductivity as well as mechanical properties, etc. The parameter is not so much informative for microsystems and especially for nanoscale systems. At the same time, such parameters as radial pore size, the density of their distribution, and growth direction are important on their own, although they rather describe the type of PS layers in the form of individual pores in the shape of a well and do not characterise any PS layers of other types. The International Union of Pure and Applied Chemistry (IUPAC) has accepted the size factor as the "classification parameter" of PS, so the pores are categorised by their size (micropores (d < 2 nm), mesopores (d = 20÷50 nm), and macropores (d > 50 nm)) [7, 8]. In our opinion, this classification is surely useful from the point of view of express classification of PS and is widely used in scientific literature, but it considers only its well-shaped structure and the underlying classification parameter of the radial pore size. This does not take into consideration such important parameters of PS layers as density of pore distribution, layer thickness, pore growth direction, and others. This does not allow determining general integral properties of PS layers and drawing conclusions about the possibility of their functional use. In fact, we can state that currently there is no integral feature that can characterise all or at least most types of PS layers.

2. Analysis of the parameters used in studies on porous silicon

PS layers have relatively varied structures [9] that depend both on the conditions of their production (duration of etching, current density, etching reagent composition, etc.) and on the parameters of the initial silicon (conductivity type, impurity type and concentration, crystallographic orientation of the initial silicon wafer, etc.). These parameters determine the places of the origin of pores and influence their development as well as the formation of layers with different morphology, for example, in the form of individual well-shaped pores, coral-like threads, rods, and other similar formations. Taking in consideration the aforementioned, we believe it is reasonable and important to choose some integral PS-characterising parameter which would indicate the specific features of almost all the formed layers while not depending much on their individual structure and morphology.

PS layers of any modification are characterised by a highly-developed surface of nanostructured layers being formed that in most cases are responsible for the practical significance of PS in the majority of the areas of practical use of PS (adsorption, medicine, energetics, etc.). It should be taken into account that the surface formed during the electrochemical etching of silicon contains different atomic groups such as Si-H_n, Si-OH, Si-O-Si, etc. [10] that can participate in various physicochemical processes determining the functional properties of the materials.

Thus, based on the aforementioned, we believe that the integral parameter is the total specific inner surface of PS which is able to characterise various obtained materials without specifying their structural individuality. The detailed

description of the types of characterisations of porous objects is presented in [11]. Total specific inner surface is often used when describing different porous materials. However, this parameter is very rarely used in the works related to porous silicon. This can be due to the fact that it is very laborious to determine it, and authors of the studies believe that this parameter can be fully replaced by porosity. At the same time, as it was mentioned above, a great number of properties of porous silicon depend on the behaviour of the pore surface, and the parameter we propose, the specific inner surface, seems to reflect the properties of porous silicon more comprehensively. This parameter surely depends on radial and axial pore sizes as well as the density of their distribution, as it contains the part of the total inner surface of PS that corresponds to these formations. Unlike the classification feature of IUPAC, this one allows characterising PS not by a particular parameter (radial pore size) but by the parameter that indicates the most important property for the use of this material which has a certain numeric value even in case when the pores of all size ranges from the IUPAC classification can be found in a PS layer at the same time.

The introduction of the parameter of total specific internal surface for the characterisation of PS is reasonable due to the fact that a great proportion of atoms in nanosized formations are located on the surface of particles and they participate in the implementation of surface phenomena. Table 1 shows these changes in the fraction of surface atoms depending on the number of atoms in the volume [12].

Table 1. Dependence of the fraction of surface atoms on the number of atoms in the volume of particles [12]

The number of atoms in the volume, cm^{-3}	10^6	10^5	10^4	10^3	10^2
Fraction of surface atoms, %	4	9	19	40	86

When the number of atoms in the volume decreases (that is, when the size of a particle decreases) from 10^6 to 10^2, the fraction of surface atoms increases to 86 %. The number of atoms in the volume 10^4 approximately corresponds to the lower size of a nanoparticle (2 nm). This is the state that determines an additional excess of surface energy, the so-called size effect typical for nanoformations.

The suggested classification parameter is the ratio of the total inner surface of PS to the volume of the etched material, and it has the dimension of the inverse length (cm^{-1}). The total area formed by the etching of the surface can be determined by the standard method of nitrogen porosimetry, and the volume with due consideration of density is calculated through the weight of silicon after etching which can be determined by a simple gravimetric method of weighing.

It should be noted that it is reasonable to use the suggested parameter not only because it can characterise PS in various fields of application, such as energy, sensory studies, optoelectronics, medicine, pharmacy, and biology, but also because it can classify and characterise the obtained nanoparticles based on PS. The practical significance of the suggested classification parameter can be confirmed by the analysis of scientific literature where, in addition to the IUPAC classification, the parameters related to the total specific internal surface of PS are used directly or indirectly [13–30].

It is reasonable to use this parameter for the classification of PS by its numeric values that determine the area of greatest effectiveness of application of this material. Such classification may include, for example, the display area of a quantum size effect (optoelectronics), or the area determined by the value of specific surface depending on the linear pore sizes or the density of their distribution (sensory studies and medicine), etc.

3. Conclusions

The introduction of a new classification feature, the total specific internal surface of PS layers, as an integral feature will allow defining the special characteristics and properties of various PS layers more comprehensively. The greater difficulty of its determination, as compared to the traditional parameters described above, is compensated for by its greater informational value, which makes it more preferable compared to other features. The use of this value does not exclude the use of other parameters for a more detailed classification.

Author contributions

All authors made an equivalent contribution to the preparation of the publication.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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Information about the authors

Andrey M. Khort, PhD in Chemistry, Associate Professor at the B. A. Dogadkin Department of Physics and Chemistry of Materials, MIREA – Russian technological university, Institute of Physics and Technology, Moscow, Russian Federation; e-mail: poristsil@yandex.ru. ORCID iD: https://orcid.org/0000-0001-8931-1793.

Anatoliy G. Yakovenko, DSc in Technical, Full Professor, Professor at the B. A. Dogadkin Department of Physics and Chemistry of Materials, MIREA – Russian technological university, Institute of Physics and Technology, Moscow, Russian Federation; e-mail: anavenko@yandex.ru. ORCID iD: https://orcid.org/0000-0001-9152-6566.

Yury V. Syrov, PhD in Physics and Mathematics, Associate Professor at the B. A. Dogadkin Department of Physics and Chemistry of Materials, MIREA – Russian technological university, Institute of Physics and Technology, Moscow, Russian Federation; e-mail: yvsyrov@yandex.ru. ORCID iD: https://orcid.org/0000-0003-2226-5790.

Received 9 June 2021; Approved after reviewing 8 July 2021; Accepted for publication 15 August 2021; Published online 25 September 2021.

Translated by Marina Strepetova
Edited and proofread by Simon Cox