

# The study of porous silicon powders by capillary condensation

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**Abstract.** Gas adsorption and capillary condensation phenomena were studied in powders of porous silicon with different doping levels of the silicon substrate of *n*-type conductivity in various conditions. Specific surface area and the rated pore size distribution were determined for porous silicon with complex texture by the capillary condensation method. It is shown that the samples obtained in silicon with a higher doping level have a higher value of specific surface area.

## 1. 1. Introduction

Materials with a high porosity are widely used for sensors, in medicine, as catalysts, radar absorbing, sound and heat insulating coatings for solving problems of component storage, in alternative energy systems of hydrogen storage and so on. Porous silicon (por-Si) and por-Si powders are one of the most promising advanced materials in medicine (targeted drug delivery, implants, photodynamic therapy, biosensors, etc.) [1–4]. The extremely important factors for nanocontainers are geometric characteristics and surface properties of the porous material. The appropriate research methods are required to control the geometric characteristics of the porous silicon and to study the mechanisms of interaction with various substances (conditions of adsorption/desorption, selectivity) with the introduction of one or more drug molecules, fullness, etc.).

In [5] there is an overview of modern methods for the structural study of porous materials. According to [5], the methods for the characterization of the pore structure can be classified according to three basic physical principles they are based on. The first class of methods includes various methods of microscopy providing direct observation of the surface or the cleavage of the studied material. They include scanning electron microscopy, transmission electron microscopy, various techniques of the scanning probe microscopy and others [6]. The second class includes nonpenetrating control methods which are based on the phenomena of scattering of radiation and propagation of waves, positron lifetime spectroscopy [5], and so on. These methods are generally used for the analysis of both open and closed pore systems but require expensive equipment and complex mathematical processing results. Among the third class that includes penetrating analysis methods there are the methods associated with the phenomena of gas adsorption, mercury porosimetry and calorimetric methods.

Adsorption research methods can be considered as the most common way to analyze the material's porous structure. Direct adsorption measurements can be carried out under static conditions, when the



transfer of the adsorptive on the solid surface takes place due to diffusion. If the transfer of the adsorptive on surface of the solid is carried out by a flow of the carrier gas, these methods are referred to as flow-through adsorption measurements or dynamic. These methods are widely used in rapid measurements. This investigation method is realized in the devices “Sorbi”, in particular, in the device “Sorbi MS” used in this work. The advantage of the method is the possibility to test a sample nondestructively without using toxic substances. The disadvantage of the technique is the possibility to study powders only and using the mathematical models in arriving at parameters of the porous structure.

It should be noted that there are advantages and disadvantages for all of these methods. A full investigation of all sizes of porous is only possible by using several independent methods.

In this work the investigation of porous silicon powders (PSP) obtained by electrochemical etching in *n*-Si (111) was carried out using gas adsorption and capillary condensation.

## 2. Experiment

Por-Si powders were obtained in one-chamber electrochemical cell in an aqueous solution of hydrofluoric acid and isopropanol mixture with the addition of hydrogen peroxide [7]. The choice of process conditions (anodization current density of  $j = 70 \text{ mA/cm}^2$ , anodization time of  $t = 25 \text{ min}$ ) was determined by the requirement to obtain mesopores and based on the experience of previous studies [5–7]. As a raw material, the single crystal *n*-Si (111) with a resistivity of 1.0 and 0.3  $\Omega \cdot \text{cm}$  was used. The por-Si samples thus obtained were then subjected to sonication, and thus yielded a powder of por-Si.

Gas adsorption and capillary condensation measurements were provided by means of SORBI MS (“META”, Novosibirsk), software SoftSorbi II, that realizes physical adsorption of noble gas by the sample to be studied. The device SORBI MS allows one to explore the systems with different pore size: to measure the total specific surface according to the method Brauner, Emmett, Teller; to measure the external surface area (“external” means without micropores as they are filled with liquid adsorbate) and to evaluate the specific micropore volume; to investigate the processes of capillary condensation in mesopores and to receive information about the distribution of the mesopore sizes.

The features of the method are discussed in [8, 9] concerning the study of the porous sol-gel system “silicon dioxide - tin dioxide”. Operating principle of the instrument is based on the comparison of the volume of the gas-adsorbate which is absorbed by the studied sample with the volume of the gas absorbed by the standard sample with a known value of specific surface area. A standard sample was used for calibration of Sorbi. The standard sample has globe-shaped granules (the diameter is 2 mm, the weight is 0.01 g) and its specific surface area is 67  $\text{m}^2/\text{g}$ . Nitrogen was used as a gas-adsorbate, and helium was used as a carrier gas. For the measurement of absorbed gas volume the thermal desorption method was applied. The specific surface area was calculated according to the model of Brunauer, Emmett, Teller. Before the measurements the samples were heat treated using SorbiPrep station.

## 3. Results and discussion

In this paper two series of PSP were obtained under the same conditions but with the use of silicon substrates with different resistivity: *n*-Si (111) with 1.0 and 0.3  $\Omega \cdot \text{cm}$  (series I and II, respectively). Prior to the measurements, a probe of PSP was weighed on an analytical balance (CE124-C, SARTOGOSM). Before gas adsorption measurements, the samples surface was purified from impurities by heating in the sample preparation station SorbiPrep®. Degassing was carried out by heating the sample in a stream of inert gas prior to the determination of its specific surface. Further, the ampoule with the test sample was loaded into the adsorber.

Selection of thermal treatment parameters is important because it affects the accuracy of determining the specific surface area of the sample. If any impurities or the condensed water from the environmental atmosphere remain on the surface, the experimentally determined value of the specific surface area is lower than it should be. On the other hand, the thermal treatment conditions

(particularly, temperature) must not alter the structure of the porous silicon. It is known that temperature treatments above 450–500°C in some types of porous silicon could cause the coalescence. Effective degassing conditions will vary depending on the material composition and geometrical properties (pore size, their channel shape, porosity, etc.). The conditions of thermal treatment (thermal treatment time and temperature) were experimentally determined using series I. For series II with higher expected values of the pore diameter the capillary effect is less pronounced, so the adsorbate can be removed easier. Thus, the conditions of thermal treatment chosen for the samples with smaller pores (series I) will be also effective for the samples with larger pores (series II).

To select the suitable conditions for thermal treatment, the specific surface area of the porous silicon powder Type 1 was measured by the gas adsorption method at 4 different combinations of pairs of parameters. The treatment time was 45 and 90 min, and the temperature was 150, 300 and 350°C, and also without any thermal treatment. The results are shown in table 1. According to the measurements of specific surface area for the same sample of series I prepared at different thermal treatment (table 1), the following thermal conditions were selected:  $t = 90$  min,  $T = 350^\circ\text{C}$ . These conditions were used as well for measurements of samples of series II.

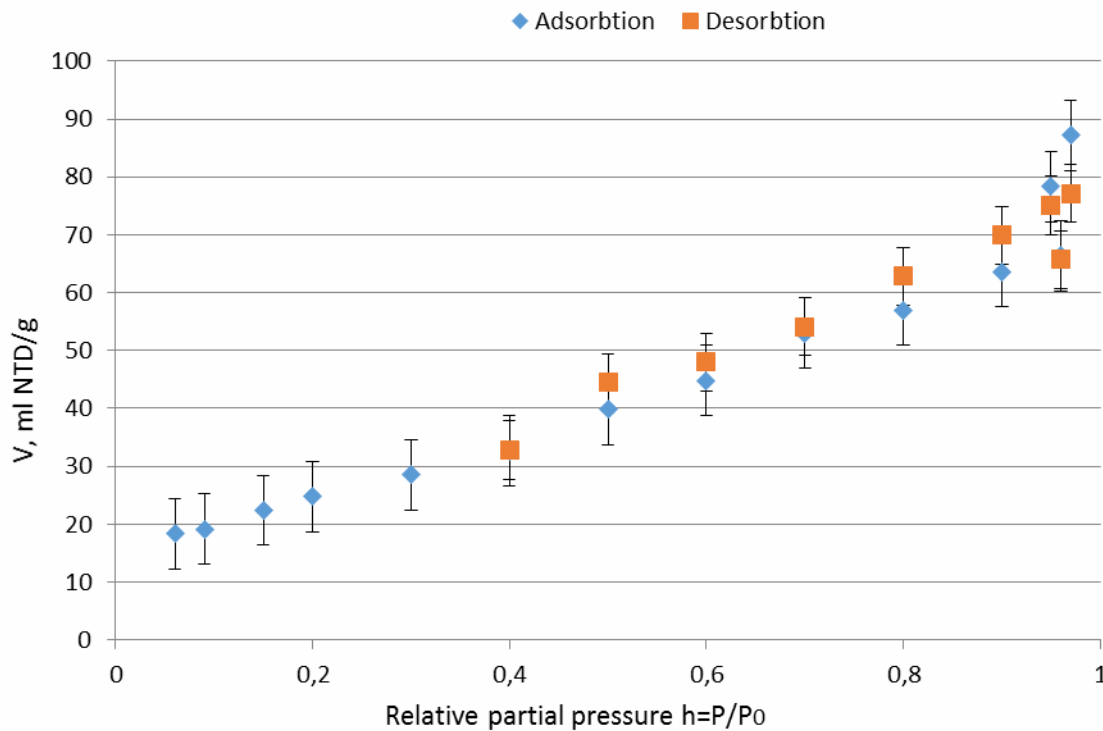
**Table 1.** The data on the specific surface area for the por-Si powder calculated by the BET method

| Series of samples | Specific resistance of silicon wafer, $\Omega\cdot\text{cm}$ | Mass of sample $m$ , mg | Preparation time $t$ , min | Temperature of the preparation $T$ , $^\circ\text{C}$ | Measurement technique; 1 – BET 2 – full adsorption / desorption isotherms | The specific surface area, $S$ , $\text{m}^2/\text{g}$ |
|-------------------|--|-------------------------|----------------------------|---|---|--|
| I                 | 1.0  | 10                      | without treatment          | without treatment                                     | 1   | 54.28  |
|                   |  | 10                      | 45                         | 150   | 1   | 49.6   |
|                   |  | 32                      | 45                         | 300   | 2   | 91.63  |
|                   |  | 32                      | 90                         | 300   | 1   | 87.4   |
|                   |  | 32                      | 90                         | 350   | 1   | 104  |
| II                | 0.3  | 18                      | without treatment          | without treatment                                     | 1   | 195.2  |
|                   |  | 18                      | 90                         | 350   | 1   | 201  |

Comparison of the specific surface area  $S$  in the samples of different series showed that  $S$  in series II (the por-Si powders obtained under the same conditions but in silicon with a lower resistivity) is almost twice higher than  $S$  in series I: 104 and 201  $\text{m}^2/\text{g}$  respectively. Apparently, the dependence of  $S$  on the conditions of heat treatment for the samples of series I is stronger due to the presence of smaller pores, the removal of condensate from which requires a higher temperature and a longer exposure time in the thermal treatment station. The samples of series II seem to possess pores of larger diameter, and the condensate layer has less effect on the value of  $S$ . A larger specific surface area of the samples of series II results probably from the greater depth of gas penetration (due to larger pore channels), thus involving more volume of porous silicon powder particle into adsorption. In samples with smaller pores (series I) adsorption occurs primarily in the surface layers.

Pore size distribution by capillary condensation was determined for the samples of series I. The algorithm for calculating the full adsorption isotherm was carried out using the device SORBI MS.

Figure 1 presents the full adsorption/desorption isotherm with a relative error method, which is 6%. This adsorption/desorption isotherm was analysed with the use of software SoftSorbi2. The results are shown in table 2. As seen from the table, por-Si of the studied type possesses mesopores with the size varying from about 3.5 nm to 56 nm. It should be noticed that there are pores of small diameter (less than 5 nm), the proportion of which was 42.4% of the total pore fraction. Also there are pores with the size of 10–20 nm and 50 nm.



**Figure 1.** Full adsorption/desorption isotherm for the sample of por-Si formed in *n*-Si (111)

**Table 2.** Size of pores for the por-Si powders (series I) taken by full adsorption/desorption isotherm

| $D_i$ , nm | $V_i/V_{total}$ , % |
|------------|---------------------|
| 3.5        | 34.5                |
| 4.4        | 7.8                 |
| 5.9        | 14.2                |
| 8.4        | 19.1                |
| 15         | 5.3                 |
| 56.1       | 19.1                |

#### 4. Conclusions

Thus, the specific surface area of PSP was measured by gas adsorption method. It is shown that under the chosen conditions a decrease in resistance of *n*-silicon substrate results in a substantial increase in the specific surface area of the porous silicon powder (201 and 104 m<sup>2</sup>/g for Si wafer with 0.3 and 1.0 Ω·cm specific resistance respectively). For PSP prepared from silicon (1.0 Ω·cm) the pore size distribution was determined. PSP of series I obtained at the selected conditions of electrochemical

anodization possesses mesopores of different sizes: pores with the diameter less than 5 nm (the proportion of which was 42.4% of the total pore fraction) and rather larger mesopores with sizes of 10-20 nm and 50 nm. It was shown that the capillary condensation method enables one to determine the pore sizes in the porous silicon with a complex porous structure (2 or more types of pores, micro- and mesopores).

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