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Investigation of helium charged beams passing through the porous alumina membranes

E N Muratova¹, A A Shemukhin²

¹Saint Petersburg Electrotechnical University "LETI", ul. Prof. Popova, 5, Saint Petersburg, 197376, Russia
²Skobeltsyn Institute of Nuclear Physics, Moscow State University, 1(2), Leninskie gory, Moscow, 119991, Russia

E-mail: sokolovaetnik@yandex.ru, shemuhin@gmail.com

Abstract. Membranes of nanoporous aluminum oxide (alumina) have been obtained using the electrochemical etching technique by varying technological regimes. They were investigated by the Rutherford backscattering technique. The obtained spectra revealed distribution of elements over the entire thickness of the layer. It has been shown that almost all ions, which fly in the beam, fall into the channel - por Al₂O₃. This leads to a focusing of the charged particles beam.

1. Introduction

Over the past years, scientific interest in the creation and study of nanostructures has increased. Nanostructures are of practical and scientific interest to understanding the fundamental electronic, magnetic, optical, thermal and mechanical properties of materials with nanometer dimensions characteristic elements, and also to creating devices with previously unattainable parameters. Beams of charged particles, which are finding wide application in both fundamental studies and solving applied problems (e.g., in technology and in medicine), are attracting also great interest at present [1, 2]. A series of recent works [3–5] consider the possibility of transporting beams of accelerated charged particles via dielectric channels without energy loss and loss of the initial charge state.

To date, a number of effective methods of creating nanostructures is developed, and among them methods based on the principle of self-formation are extremely important. Nanoporous materials, of course, can be classified as nanostructured objects derived by the self-organization.

One of the most studied of structured porous materials obtained by electrochemical anodization is a porous aluminum oxide (por-Al₂O₃). The uniqueness of aluminum is in the process of electrochemical etching under certain process conditions may be obtained from self-assembled layer of Al₂O₃ pore structure of the "honeycomb". Membranes based on nanoporous alumina are required in nanotechnology, microbiology, and nuclear physics, because they have unique properties, such as mechanical strength, thermal stability, and chemical resistance.

The structure membranes based on nanoporous alumina, which has been intensely studied in recent decades [6, 7], is an ideal dielectric matrix of nanocapillaries [4]. A peculiarity of por-Al2O3 is that, during electrochemical etching, it shows the ability to self-organization and forms a structure with a given geometry when technological conditions are varied [8, 9]. Studies of using por-Al2O3 membranes as a dielectric focusing matrix, which can provide transport of beams of accelerated charged particles through dielectric capillaries, are thus of interest [10,11]. It will make it possible to perform highly local analysis of the structure and composition of samples without setting up high vacuum conditions [12, 13] and exerting topologically ordered effects on a nanosize level.

Thus, formation of mechanically strong membranes based on porous alumina with ordered capillary structure on micro- and nano-scale in a thin (~ 10 µm) aluminum foil is the actual problem.
The aim of this work was the formation of free masks—membranes with the through nanocapillaries and study possibilities of their application as nanoscale templates for high-energy ion beams.

2. Experiment
We used a well-known mechanism to formation of ordered cellular structure por-\text{Al}_2\text{O}_3 [7, 9]. To obtain por-\text{Al}_2\text{O}_3 unicameral cell to electrochemical etching with the ability to control the temperature of the system has been designed.

In order to obtain a porous anodic alumina membrane [9] the electrochemical anodization of aluminum foil (40 \mu m) was applied in a potentiostatic mode in electrolytes based on aqueous solutions of phosphoric (H_3\text{PO}_4) and sulfuric (H_2\text{SO}_4) acids for 10–60 min at temperatures from 0 to 15°C. When using electrolytes with different acidities, the speeds of an anions introduction into the porous layer are different. This effect determines the voltage of the pore formation process and consequently the pore diameter. The anodizing voltage was within the range of 15-30 V (for H_2\text{SO}_4) or 130-160 V (for H_3\text{PO}_4) depending on the electrolyte type.

The basic structural parameters, such as the pore diameters \(a\) (see figure 1), the distances between pores \(b\), the thickness of the porous layer \(c\) and the barrier layer \(d\) of the obtained samples were studied using the scanning electron microscopy (SEM) at low accelerating voltages (10–20 kV) under high vacuum, that allowed us to study the insulating samples without a prior metal deposition.

Through translucent membrane auto-fixed on aluminum substrate were obtained on aluminum foil. Membranes based on por-\text{Al}_2\text{O}_3 were obtained using the conditions of galvanostatic modes. \(U-t\) curves have a typical shape characteristic of the processes of electrochemical oxidation is illustrated in Fig. 2. The sharp rise in voltage on the curve is due to complete oxidation of the aluminum foil and through membranes formation based on por-\text{Al}_2\text{O}_3. It should also be noted that the anodizing current increasing in twice result in the anodizing time reducing approximately doubled.
Figure 2. Galvanostatic curves of system Al / electrolyte.

During the anodizing it is necessary to maintain the process temperature (depending on the electrolyte used) to avoid the dissolution of oxide formed by acidic electrolyte. It is possible to control the thickness of the porous layer and alter its mechanical properties by controlling the temperature during the anodizing process. In this work the optimal temperature of the process for different electrolytes supported in according to Table 1.

| Electrolyte | H₂SO₄ | H₃PO₄ |
|-------------|-------|-------|
| The voltage of generation, V | 5–25 | 60–120 |
| Process temperature, °C | 20 | 0–2 |

To conduct research using the Rutherford backscattering technique (RBS) it was established a special experimental chamber (Fig.3), which includes a collimating aperture, a system of detection of backscattered ions and using a goniometer system. The diameter of the ion beam after passing through the system aperture is 1 mm. Residual pressure in the chamber did not exceed 5·10⁻⁴ Pa. The current density on the target was maintained constant and amounted to 4 nA.

The sample is installed in the chamber on the goniometer system. The goniometer provides the rotation of the sample around all three axes and translational movement in a vertical direction, allowing to measure different portions of the surface of the sample without changing orientation relative to the beam. The angular displacement can be made using a stepper motor, and angular displacement is made using stepper motors, the rotation is carried out with a step of 0.02°. The inaccuracy of the execution of the turns at large angles does not exceed 1%. The angular position of the detector relative to the target can be changed in the scattering plane on a circle which center coincides with the center of rotation of the goniometer.

To study the passage of a beam of ions He⁺ through the oxide matrix were used the RBS technique in combination with channeling. For this purpose, the beam diameter of 1 mm was directed onto the sample surface. With the manipulator in the horizontal plane α the angle of incidence of the probing beam ions was installed α = 7 and the spectrum of RBS sample was recorded in the absence of channeling. Then the angle x speed was decreased, and at each step the energy spectrum of RBS was recorded.
When the RBS spectra of membrane were detected, a detectable scattering angle was 165°. The semiconductor detector filmed how the signal passed through the membrane of ions of He⁺ ions and backscattered ions.

3. Results and discussion

Obtained membranes were studied using the RBS. The RBS technique was used for in situ determination of the optimal geometry of the experiment. First, the position of a semiconductor detector at which the yield of the backscattered ions is uniform and minimal was found. This case corresponds to the situation when the pores in the target are through. It is worth noting that the above-mentioned ion-beam method of controlling the quality of nanoporous membranes structures is nondestructive.

The RBS spectra (figure 4) show the dependence of the number of passed particles on the slope angle of the target for the membrane containing pores of about 20 nm in diameter.

In the virgin structure close to the 400 channel (curve A), the peak of oxygen, which corresponds to the natural oxide, is observed. The thickness of the layer with disordered atoms of aluminium allows to estimate it at about 5–7 nm. The RBS spectrum of the porous membrane consists of two of flat

![Figure 3](image3.png)

**Figure 3.** Schematic representation of the experimental process.

![Figure 4](image4.png)

**Figure 4.** The energy spectrum of backscattered He⁺ ions with the energy of 1.7 MeV for the scattering angle of 120°. A – the structure of aluminum without etching, B – after electrochemical etching [14].
portion, indicating the formation of a uniform oxide layer on all the analysis depth. However, it appears that the por-Al₂O₃ structure contains not only the basic elements (oxygen and aluminum), but also sulfur. After etching, an extra peak in the high energy part of the spectrum (curve B) occurred which corresponds to backscattered He⁺ ions from sulfur. It is distributed rather evenly throughout the depth of the membrane, with some maximum concentration near the surface. The concentration by volume may achieve 16% close to the surface. The appearance of this impurity may be due to the foil quality, the results of washing samples after anodic oxidation, and the possibility of acid anions incorporated into the formed oxide. The increase in the yield of backscattered ions with decreasing energy is due to the dependence of the backscattering cross-section from energy.

Membranes, in which there are additional ions, are not suitable for beam focusing effect. For example, the presence of sulfur ions promotes charge leakage, instead of forming a focusing channel. For guading - effect the dielectric matrix should have a rather high resistance, since such beams transportation is provided by charging of the inner walls. However, the data of the membrane suitable for transporting bundles of high-energy charged particles. In this case, the transportation may be provided by the mirror reflection ions emitted at grazing angles, that is, due to small-angle scattering.

It should be noted that Rutherford backscattering technique in combination with channeling can be used for analyzing the transmission coefficient of oxide matrixes. Figure 5 shows RBS spectra of backscattered ions at different position of the sample. The RBS spectra were recorded in two directions: when the beam was parallel to the pores in membranes (curve B), and in directions didn’t contain open channels. In the case when the direction of incidence of the ion beam coincides with the direction of the pores, there is a minimum yield of scattered ions as a result of the passage of the ions into the sample. Fig. 5 show that when orientation of the alumina membrane is perpendicular to the analyzing beam to fall (curve B), then output backscattered ions decreases sharply in 14 times, compared to the direction that didn’t contain open channels (curve A). This demonstrates that most of the ions have flown through the membrane. The output of the backscattered ions from sulfur decreased in more than 20 times in the direction when the beam was parallel to the pores. It shows that the sulfur concentration decreases as the distance from the surface.

![Figure 5. The energy spectrum of backscattered He⁺ ions for the scattering angle of 120°.](image)

The work [14] has shown that the passage of ions through such dielectric matrix is 60–70%. However, according to figure 1, the area ratio of the pore square to the sample square is 0.2–0.3. This can be explained as follows: probably the charged particles when passing through the membrane create a potential on the dielectric walls of the pores (channels). Thus, the fraction of the particles goes immediately into the channel, and the part deviates from the initial direction and into the channel.
potential dielectric matrix. This situation leads to the good focusing of a beam of charged particles, which can be used in nanolithography. Thus, using the RBS technique for investigating nanoporous alumina membrane allows to “in situ” control of change structure by the action of ion irradiation. The beam current is controlled by a potential.

4. Conclusion
Thus, the technology of producing self-forming porous membranes has been proposed. The porous membrane is a system of ordered nanoscale (pore diameter of 20 nm or more) alumina capillaries with an aspect ratio of 500.

The RBS results have shown that using of sulfuric acid as electrolyte during the anodizing process results in the incorporation of sulfur anions in the membrane structure throughout its thickness. These data are confirmed by X-ray microanalysis. The presence of sulfur makes the membrane not suitable for the transport of low energy charged particle beams. It is noted that using of phosphoric acid as the electrolyte is not conducive to the incorporation of impurity anions in the depth of the membrane. Therefore, such structures are attractive at creating of mask for ion lithography.

We propose to monitor the change of the membrane structure in the mode of “in situ” by the action of the ion irradiation using the RBS technique combined with channeling. It was found that the increase of the output of backscattered ions in the direction of channeling leads to degradation of the membrane pores.

It is shown that the nanoporous membranes based on alumina containing a nanoscale capillaries system provide the transport of high-energy flow of helium ions with energy of 1.5–2 MeV.

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