Regular Polymer Microporous Membranes: Manufacturing by Deep X-ray Lithography and Possible Applications

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Abstract

The X-ray lithography at the VEPP-3 storage ring was applied for fabrication of polymer microstructures with sub-micrometer sizes of elements and with rather high aspect ratio (up to 20). The microstructures are the regular microporous membranes with pores of 0.3-0.5 μm in diameter arranged with a 1 μm spacing. The membranes were fabricated on a base of 2.5, 3, 6 and 10 μm-thick mylar films. In contrast to the commercial track membranes with random pore locations, the regular membranes have no dispersion of pore sizes caused by confluence of adjoining pores. The membranes have a porosity of 10 - 20 % and this value can be increased up to 50 % and higher by using an X-ray mask with an appropriate pattern. The results of the membrane examination by scanning electron microscopy, by gas conductance measurements, and by measurements of penetrability for micro particles and bacteria cells are presented. Possible improvements of the membrane parameters and some potential applications of the membranes are discussed.

I. INTRODUCTION

Polymer microporous track membranes are well known, commercially available and widely used in many fields due to their doubtless merits (1). The membranes are made by irradiation of polymer films by heavy ions or fission nuclear fragments with the use of heavy ion accelerators or nuclear reactors. The original tracks of the particles in the film are the sites of polymer structure modifications. Post-treatment of the irradiated polymer films by suitable etchants produces through holes of sub-micrometer size at the track locations.

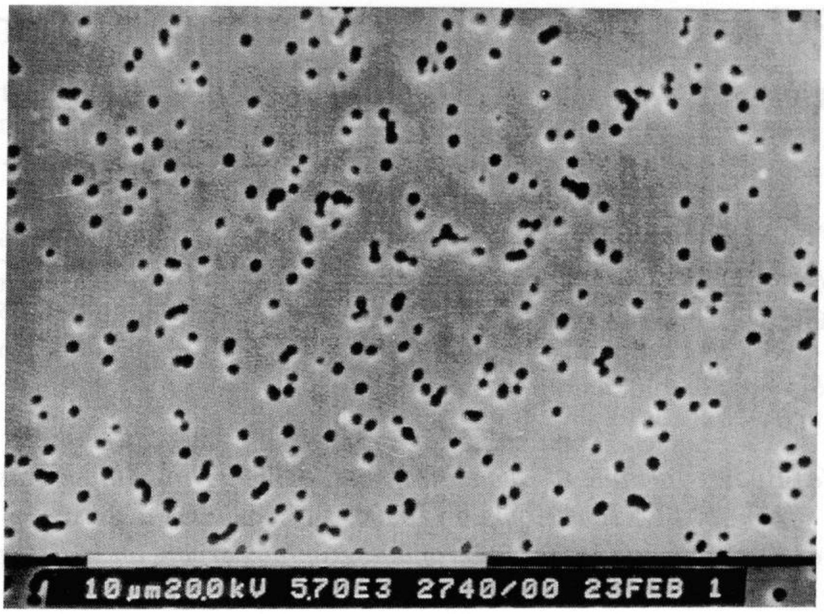

Fig. 1. A SEM photograph of a traditional track membrane based on 8.5 µm-thick polymer film with a 0.4 µm average size of the pores.

One of the characteristic properties of such membranes is random locations of pores (Fig.1). Due to this reason, for the commercial track membranes the effective spread of pore sizes is about ± 10-15 % and caused mainly by confluence of two or more adjoining pores. Usually, a typical porosity of the membranes does not exceed 10 % because the higher value of porosity leads to the higher dispersion of pore sizes. This is essential demerit of the membranes.

Basing on the similar principles of the membrane fabrication and using a deep X-ray lithography technique it is possible to produce microporous membranes with regular arranging of uniform sub-micrometer pores. Such membranes can have a high porosity (50 % or higher) in combination with a high uniformity of the pore sizes. These membranes have no dispersion of pore sizes caused by confluence of adjoining pores. Due to their valuable properties, the regular membranes can find many applications in scientific and technology fields.

The present paper describes the first experience on the manufacturing and examination of the prototypes of polymer regular membranes with sub-micrometer pore sizes. Potential improvement of the membrane parameters and the membrane capabilities for possible applications in different fields are discussed as well.

II. FABRICATION PROCEDURE

At present a number of prototypes of the polymer microporous regular membranes with sub-micrometer pores has been fabricated at the Budker Institute of Nuclear Physics (Novosibirsk, Russia) (2). The fabricated membranes are based on the mylar films of 2.5, 3, 6 and 10 µm-thickness. An example of the fabricated prototype of the regular track membrane is shown in Fig.2.

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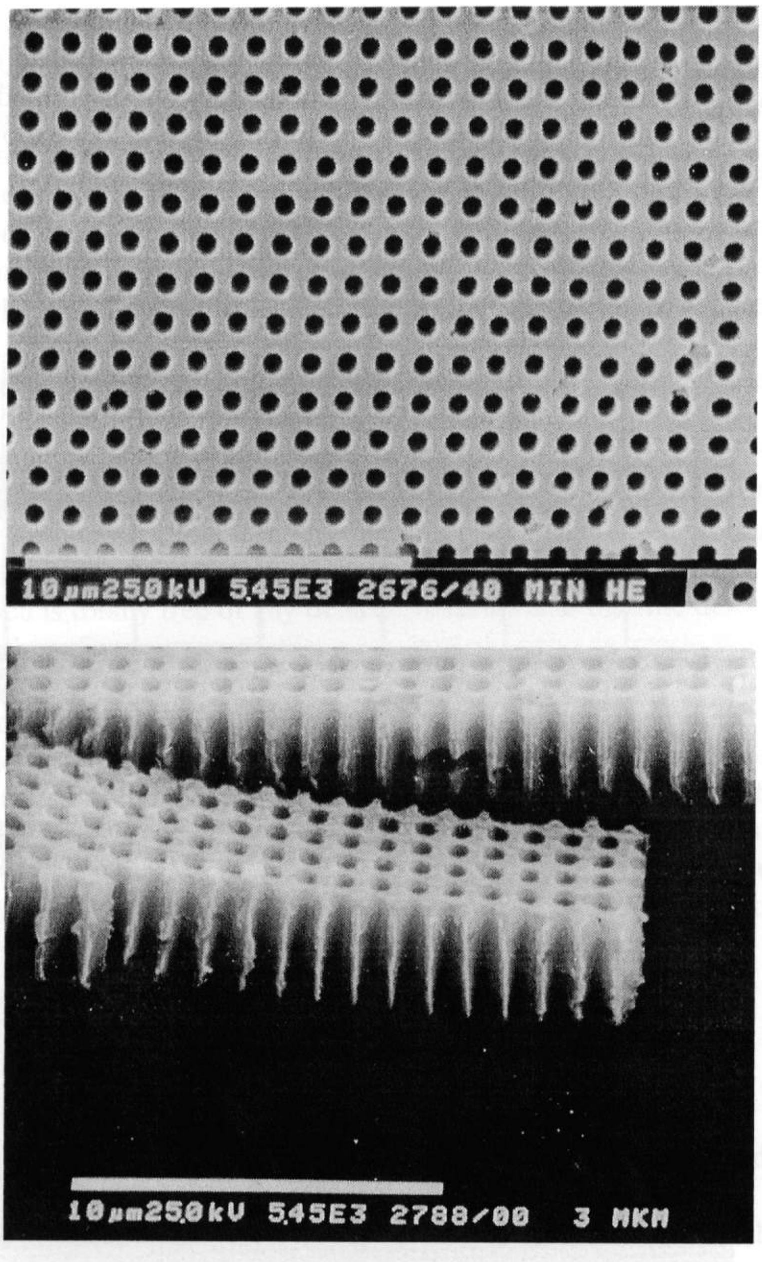

Fig. 2. SEM photographs of the 3 µm-thick mylar regular membrane (0.5 µm pore diameter and 1 µm spacing); (a) - top view, (b) - cross section of the membrane.

The process of membrane fabrication includes the operations of an exposure of the mylar film by an X-ray beam through the X-ray mask with an appropriate pattern, an etching of the exposed films in a water-alkaline solution and a washing. A mylar film itself is used as an X-ray positive resist. The conditions of the film processing, such as the concentration and the temperature of the etchant, as well as the etching time were found from the measurements of the film etching speed versus the X-ray exposure dose. The pore diameter is determined by the original pattern of the X-ray mask but the conditions of the film processing allows one somewhat to vary pore sizes.

The X-ray exposure of the films with the use of synchrotron radiation is performed on the X-ray lithography station of the VEPP-3 storage ring (3). At the 1.2 GeV electron energy of the storage ring which is normally used for the lithography works; the station provides irradiation in the 0.3 - 1 nm spectral range. This range allows us to perform a deep X-ray exposure of polymer films with a total thickness of up to 20 μm.

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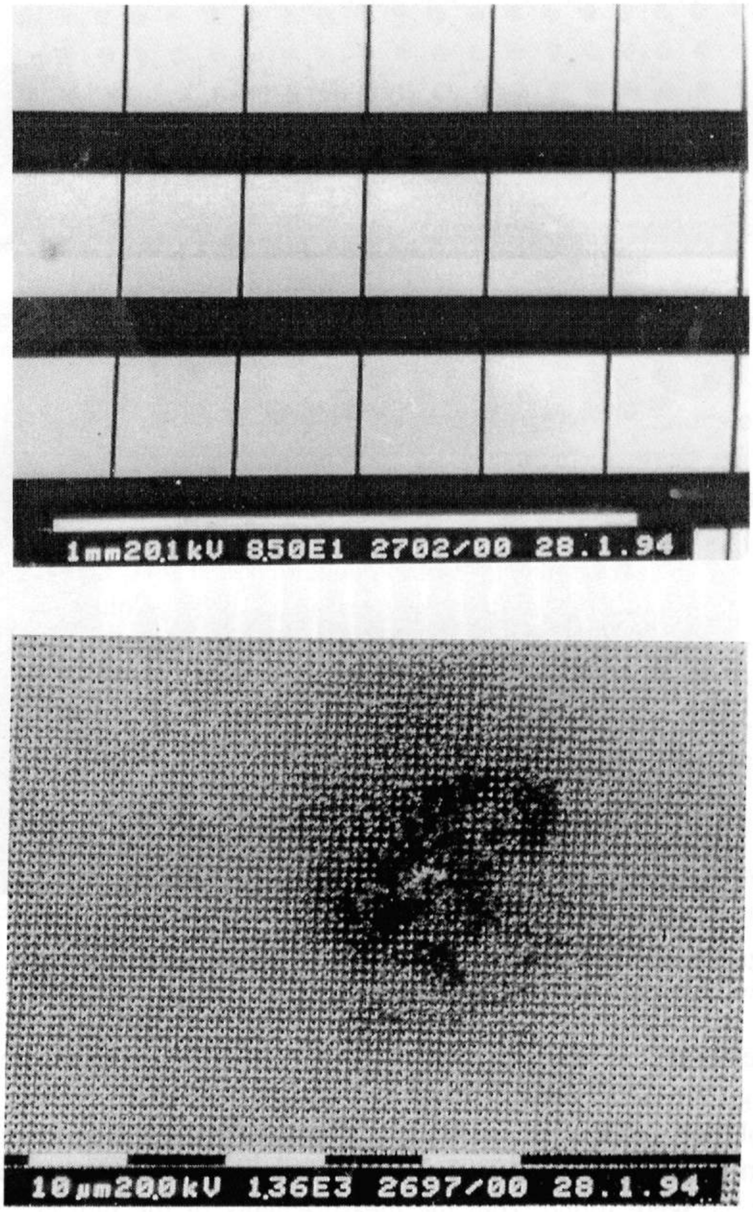


Fig. 3. Structure of the X-ray mask pattern; (a) - squares with holes (white) and reinforcing hole free strips (black), the arrow indicates the site of repaired defect, (b) - large scale view of a square area with holes and with the repaired defect of a kind of puncture.

An X-ray mask for membrane fabrication is made by electron beam lithography on the base of a 2 μm-thick silicon membrane and an 0.9 μm-thick electroplated gold absorber. Under the conditions of the lithography station operation indicated above, the X-ray contrast of the mask is not less than 10. The working rectangular area of 25×2.3 mm ^{2} of the mask is composed of squares of 200×200 μm ^{2} separated by reinforcing hole-free strips (Fig.3). Every square is filled by pore holes arranged as a two-dimensional grid with a 1 μm spacing in both directions. The reinforcing strips have 10 μm width along the long direction of the rectangle, and 100 μm width along the lateral direction. The pore diameter is quite uniform along the long rectangular direction and changes roughly linearly in the lateral direction from 0.35 μm at one side of the rectangle to 0.5 μm at the other side.

The lithography station provides a single exposure over the 25×10 mm ^{2} area at a time and a total exposed area of 25×40 mm ^{2} with the use of a multiplication procedure. The most of the fabricated membrane prototypes have a porous area of 25×2.3 mm ^{2} replicating the working field of the X-ray mask. In addition, a number of prototypes with a 3-5 multiplication of the mask pattern were fabricated as well for investigation of the membranes with an increased working area.

It seems very problematic to fabricate an X-ray mask with a pattern of such a kind and with a large working area which is totally free of any defects. It seems also that the defects of pore absence in a limited number of confined areas of the mask pattern only decrease slightly a geometrical transparency of the fabricated membranes, and are not too essential. In opposite to this, the presence of punctures which sizes are larger than a diameter of normal pore holes, is extremely undesirable when the fabricated membranes are used as filters. For this reason, a special attention was paid to correction of such defects. A limited number of the mask absorbing layer defects of a kind of punctures was repaired by rhenium using the technique of laser induced chemical vapor deposition (4). Figure 3 demonstrates, as an example, a part of the mask pattern with a puncture defect repaired by rhenium. The result of the X-ray replication of the repaired area of the mask into mylar film is clearly observed in the upper left corner of Fig.4b where holes are absent.

III. EXAMINATION OF THE MEMBRANES

The fabricated prototypes of the regular membranes were preliminary examined by the techniques of scanning electron microscopy (SEM) and gas conductance measurements.

The SEM examination of the membranes and their cross sections show that the apertures of the pores are very close to circles with a quite uniform size and that the pores have cylindrical shape and pierce the whole thickness of the mylar films (2, 5). The SEM imaging of the membranes in transmitted electrons also demonstrates the passing of electrons through the film at the pore locations (2). A qualitative analysis of pore size measurements reveals a very good uniformity of the pores (± 0.02 μm) corresponding to a delta-like function of pore size distribution (5). Depending on the fabricated pore sizes, the average porosity of the membranes lies in the range from about 10 to about 20 %.

In addition to the SEM examination, the measurements of the gas conductance of the fabricated membranes were performed (2). These measurements provide the value of average porosity of the membranes. The measurements are carried out at low pressure of clean air (P ~ 300 Pa) that corresponds to the conditions of molecular gas flow. It allows one to calculate the conductance of the membranes with a rather good accuracy. The measured values of gas conductance for the fabricated regular membranes depend on the film etching conditions and on the film thickness, and are of the order of 0.05-0.1 l/s. These values are in a good agreement with the calculations and with the results of the SEM examination.

The technique of gas conductance measurements proved to be a useful approach for a nondestructive inspection of the membrane integral properties and is routinely used now for fast checking of the fabricated membranes.

No special investigations of the membrane mechanical properties have been performed up to now and this is a subject for further work. However, it was found that a 3 μm-thick membrane with a film diameter of 25 mm is capable to withstand a pressure difference of up to 3500-4000 Pa when it is used without any support. The appropriate support increases the membrane resistance up to a pressure difference of more than 1 atm.

Besides the 'technical' examination of the membranes, their testing for applications in different fields has started to reveal its advantages and disadvantages.

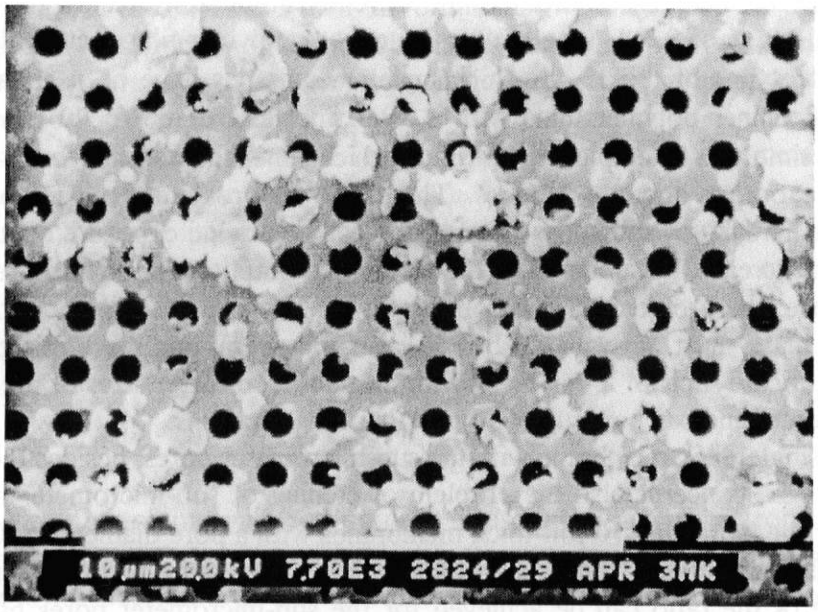
The membrane selective properties were investigated by penetrability of the vegetable and bacterial viruses with average dimensions of 0.03-0.1 μm, latex and corundum micro-spheres of 0.2-1.0 μm, and the flexible colloidal particles of the *Pseudomonas diminuta* bacteria with a 0.3 μm average particle dimension (5). A set of the membrane hole systems of different pore sizes was used for these examinations. It was shown that the model particles with average sizes of about 0.3 μm and 0.5 μm do not penetrate, practically, through the membranes with an average pore sizes of 0.32 μm and 0.54 μm, respectively. It was found also that the membrane with the 0.32 μm pore diameter retains all of the bacteria of the *Pseudomonas diminuta* family and therefore such membrane is sterilizing for these bacteria. The selective properties of the membranes with a combined hole system of 0.3-0.5 μm pores were found to be about the same as for the commercial track membranes.

The membranes were applied also, as filters, for precipitating atmospheric aerosols and suspensions in liquids followed by further X-ray fluorescent analysis for element contents (6). The membrane samples of the combined pore sizes of 0.3-0.5 μm were used for the investigations, and the obtained results are about the same as with the use of the commercial track membranes with average pore size of 0.4 μm. It means that the regular membranes can work as normal filters. The examples of deposition of aerosols and liquid suspensions on the membrane surfaces are presented in Fig.4.

All of the performed investigations clearly indicate that the fabricated prototypes of the membranes really have a regular system of uniform sub-micrometer pores crossing the total thickness of the membrane films, and that the parameters of the membranes are very close to the expected ones.

IV. POSSIBLE IMPROVEMENTS OF THE MEMBRANE PARAMETERS

The parameters and quality of fabricated regular membranes are mainly determined by the X-ray mask used for the membrane replication. Fabrication of a defect free X-ray mask with an appropriate pattern, with the sub-micrometer size elements and with a large area is not a simple task. Nevertheless, the existing level of the X-ray mask fabrication technology allows one to manufacture the required masks with a minimal size of the elements as small as 0.2-0.3 μm over the working area, at least, of several square centimeters (7). The absorbing layer thickness of about 1 μm of these masks provides an X-ray contrast which is not less than 10 for the X-ray photons with the energy allowing the exposed depth of about several tens of micrometers in polymer films. Repairing the mask defects for such thickness of the absorbing layer has been tested and the results are quite good.



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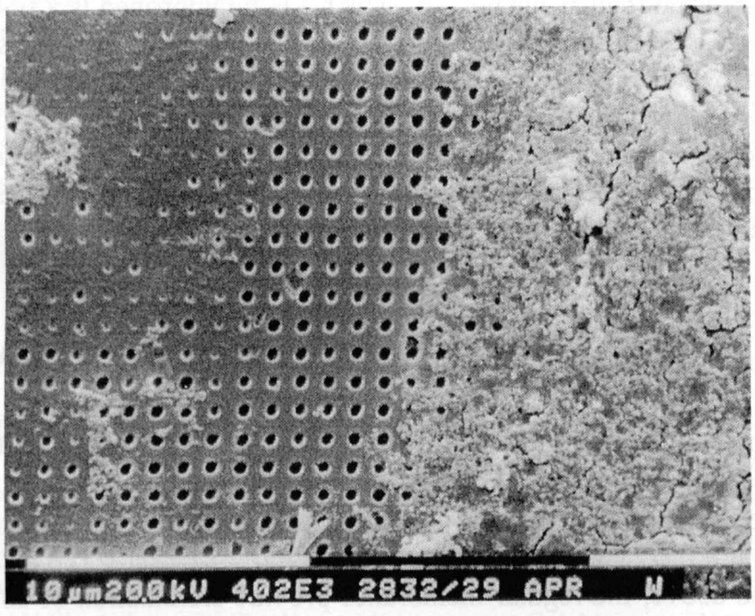

(*b*)

Fig. 4. Substances collected at surfaces of the regular membranes; (a) - atmospheric aerosol particles, (b) - water suspensions, the hole free area at the top left corner is a result of the X-ray mask defect repairing.

Basing on the acquired experience in the regular membrane fabrication and examination, it can be declared now that the desired X-ray masks must have the pores of uniform size over the total working area of several square centimeters. It would be useful also to have a set of the X-ray masks with the pore sizes of 0.2-0.4, 0.6, 0.8 and 1 μm that corresponds approximately to the average pore sizes of the commercial track membranes.

The interesting subject concerns a possibility of mass production of the regular membranes. It is not clear, at present, whether it is possible to produce polymer membranes with sub-micrometer pores using any molding process. This is a subject for further study. However, there is obvious approach to increase the membrane output using an X-ray lithography technique. The used in our experiments spectral range of 0.3-1 nm allows us to expose polymer films with a thickness of up to 20 μm, and the prototypes of the 10 μm-thick mylar membranes have been already fabricated. It means that a set of thinner polymer films with a total thickness of up to 20 μm can be exposed simultaneously at a time. For example, for the 3 μm-thick films such an approach increases, in our case, the membrane output about 6-7 times. There are no problems to use for the membrane replication the more hard X-ray radiation (0.2 nm or less) to provide exposure depth of polymers of about 0.5-1 mm and increase, by such a way, the membrane output a factor of more than a hundred. However, in this case, the problem of low contrast of an X-ray mask will appear. For rather high contrast, the X-ray mask must have the absorbing layer of several and more micrometer thickness. The possibility to fabricate such an X-ray mask with the sub-micrometer sizes of the pattern elements is problematic at present and can be a subject for further investigations.

Fabrication of a single thick membrane with the sub-micrometer pores, besides the problem of low contrast of X-ray mask, concerns also the problem of etching of sub-micrometer holes with a high aspect ratio. So, for the fabricated 10 μm-thick membranes with a pore diameter of 0.5 μm, this ratio is already 20. The thicker polymer films require the higher aspect ratio, and it is not clear now what the maximum value of the ratio can be achieved for the sub-micrometer pores by the appropriate development of the films.

The other parameter of the regular membranes which can be improved is a porosity. Geometrical considerations show that a 50 % and higher porosity can be achieved by choosing an appropriate pattern of an X-ray mask. Nevertheless, the rigidness of such membranes is a subject for study, and, probably, the optimally designed reinforcing fabric of the pore pattern will be required.

It seems also that some other polymer materials, different from mylar, can be used for membrane manufacturing. There are no doubts also that the shape of pores can be different from circles; for example, the pores can have a slit or a more complicated form.

V. POTENTIAL APPLICATIONS OF THE MEMBRANES

It seems that two main intrinsic properties of the regular membranes can be the most important for their possible applications. There are a high porosity and a high uniformity of the pore sizes. It is essential also that the membranes can have any pore size above 0.2-0.3 μm depending on the problem requirements.

As it was mentioned above, the regular membranes provide sterilization of solutions for bacteria at the certain ratio of bacteria cell size to the pore size. It means, with the account of high porosity, that a high efficiency and low temperature sterilization equipment can be developed on the basis of regular membranes for its application in biotechnology, microbiology, pharmacology and medicine.

A high uniformity of the pore sizes offers the possibility to use the membranes as standard reference membranes for certification of other types of filters and micro particles.

The use of the membranes as the substrates for substances analyzed by X-ray fluorescent elemental analysis allows us to hope for more higher sensitivity in comparison with the substrates based on the commercial track membranes. It is caused by increased effect-to-background ratio due to both the increased amount of the analyzed substance collected at a given time and the decreased mass of the substrate membrane backing. The membranes can be useful also for collecting substances whose contamination in gas or liquid medium is very low because, due to a high porosity, the collection time can be essentially decreased.

A regular arranging of the pores and their uniformity allows one to use the membranes as the high transparent and effective diffraction filters for ultraviolet and soft X-ray radiation.

In medicine, the membranes can find employment for separation of blood cells, air sterilization at treatment of respiratory diseases, burns and so on.

A high porosity of the membranes offers the possibilities for development of a high effective portable respiratory protection devices.

At present, the analogs of any membranes combining a high uniformity of the pores and a high porosity are unknown and, due to this, it is difficult to foresee all the fields of the regular membrane employment in the future.

VI. CONCLUSIONS

Traditional X-ray lithography is aimed originally at producing microelectronics chips and operates with sub-micrometer sizes of elements and thin layers not exceeding, usually, a 1 μm thickness. It corresponds to a low aspect ratio of elements (less or about 1). The first step of LIGA technology, deep X-ray lithography, uses more shorter wavelength of X-ray radiation and operates with micrometer sizes of elements of high aspect ratio (>> 1) when the thickness of layers is tens and hundreds micrometers.

The present work demonstrates that the X-ray lithography of sub-micrometer sizes can be successfully applied for producing the microstructures other than microelectronics chips. Such sub-micrometer microstructures with rather high aspect ratio (greater or about 5) may have new valuable properties and, due to this, may find many interesting and useful applications in different fields.

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