ELSEVIER

Nuclear Instruments and Methods in Physics Research A 359 (1995) 404-408

NUCLEAR INSTRUMENTS & METHODS IN PHYSICS RESEARCH Section A

Fabrication and preliminary testing of regular microporous membranes manufactured by deep X-ray lithography at the VEPP-3 storage ring

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Abstract

Regular microporous membranes with pores of 0.3–0.5 μm in diameter arranged in a rectangular grid with 1 μm spacing have been made on the basis of 2.5, 3, 6 and 10 μm thick mylar films by deep X-ray lithography at the VEPP-3 storage ring. The membranes have a geometrical transparency 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 preliminary membrane testing by scanning electron microscopy and by gas conductance measurements are presented. In contrast to the traditional track membranes with random pore locations, the regular membranes have no dispersion of pore sizes caused by confluence of adjoining pores. Some possible applications of the membranes are discussed.

1. Introduction

In the last decade the interest in using the planar technology, which has been developed for integrated circuit production, in the field of micromechanic products is increasing. In particular, the application of X-ray lithography for the fabrication of micromechanic products has led to the creation of a new manufacturing process for three-dimensional microstructures – the LIGA technology [1]. One of the distinctive features of this technology is the use of synchrotron radiation (SR) with its intensive parallel X-ray beams of short wavelength (less than 1 nm). At fulfillment of the lithography, it provides a deep penetration (more than 100 μm) of exposure radiation into a resist layer without appreciable diffraction distortions of a mask pattern with elements of submicron sizes.

Scientific research institutes and industrial companies involved in activities of the Siberian Synchrotron Radiation Center at the Budker Institute of Nuclear Physics have accumulated a considerable potential in the field of X-ray lithography for semiconductor device production. This potential allows us to apply the first stages of the LIGA technology, X-ray lithography and deep etching, for manufacturing regular microporous membranes. The main objective of this work is the development of filters with qualitatively new properties, such as a high uniformity of pore size and a high transparency, regarding the existing ones. These filters can find many applications in microbiology, microelectronics, food industry, medicine, ecology, scientific investigation etc.

The present paper describes the first experiences on the fabrication of the prototypes of mylar regular membranes with submicrometer pore sizes. The results of preliminary membrane testing are also given. Some potential capabilities of the membranes as well as their possible applications are briefly discussed.

2. Filter fabrication

The process of membrane fabrication includes exposure of the mylar film by a parallel X-ray beam through the X-ray mask, etching of the exposed films in a water-alkaline solution and washing.

An X-ray mask with a working area of 25×2.3 mm^2 was made on a 2 μm-thick silicon membrane by electron beam lithography. An 0.9 μm-thick electroplated gold

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0168-9002/95/$09.50
SSDI 0168-9002(94)01743-3

layer is used as an X-ray absorber for the mask pattern. The absorbing layer defects of a kind of punctures were repaired by rhenium using the technique of laser induced chemical vapor deposition [2]. The working rectangular area of the mask is composed of squares of 200×200 μm^2 separated by reinforcing hole-free strips. Every square is filled by pore holes arranged as a two-dimensional grid with 1 μm spacing in both directions. The width of the reinforcing strip is 10 μm along the long (longitudinal) direction of the rectangle, and 100 μm along the short (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.

A mylar film was used as an X-ray 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 exposure of the films through the X-ray mask was performed on the X-ray lithography station of the VEPP-3 storage ring [3]. The SR beamline of the station provides X-ray irradiation in the 0.3–1 nm spectral range when the storage ring operates at 1.2 GeV electron energy. Under these conditions, the contrast of the X-ray mask is not less than 10. The used spectral range allows us to perform a deep X-ray exposure of the mylar films with a total thickness of up to 20 μm. The exposure depth can be easily extended by increasing the storage ring energy, but in this case the problem of low contrast of the X-ray mask appears, and the mask with a thicker absorbing layer is required.

A number of prototypes of regular microporous membranes with submicron pores has been fabricated on a base of 2.5, 3, 6 and 10 μm-thick mylar films. All these samples had a membrane porous area of 25×2.3 mm^2 replicating the working field of the X-ray mask. Although the X-ray lithography station allows 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, these possibilities have not been employed in manufacturing the prototypes. Photographs of one of the regular membranes and its cross section are presented in Fig. 1.

a

b

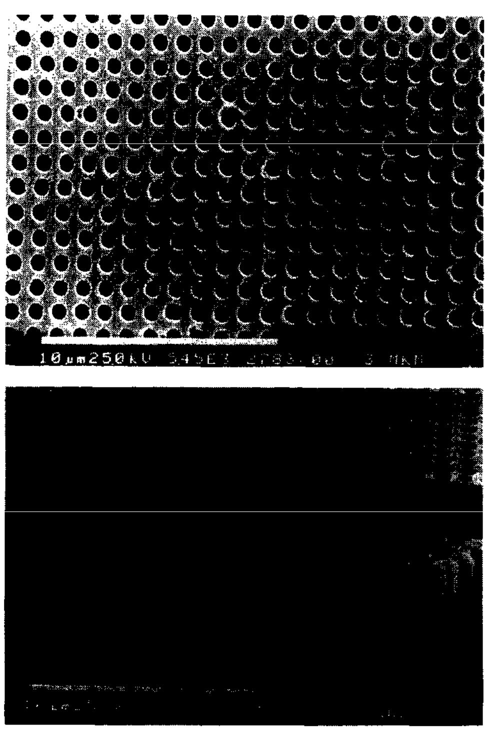

Fig. 1. SEM photographs of the 3 μm thick mylar regular membrane with 0.5 μm pore diameter and 1 μm spacing (a) and cross section of this membrane (b).

3. Preliminary examination of membranes

Many parameters of the microporous membranes are of interest for different applications, and a number of examination techniques should be used to determine these parameters. We restricted the objectives of our preliminary examination of the membranes only to a few subjects:
- to inspect the shape of the pores on the film surface and its profile inside the film;
- to ensure that the pores are the through holes;
- to measure the gas conductance for membranes and to compare the measured values with the calculated ones based on geometrical data.

One more objective is to find a simple and reliable method for technological testing of the fabricated membranes. Scanning electron microscopy (SEM) [4] and gas conductance measurements have been used in preliminary examinations.

The SEM investigations show that the surface apertures of the pores are very close to circles with a quite uniform size (Fig. 1a). The SEM photographs of the membrane cross section confirm the cylindrical shape of the pores piercing the whole thickness of the mylar film (Fig. 1b). The SEM imaging of the membranes by collecting the electrons coming through the film also demonstrates the passing of electrons in the pore locations observed simultaneously by conventional registration of secondary scattering electrons (Fig. 2).

However, all the methods of SEM investigations do not give an absolute guarantee that the pores are through ones. In the case of cross section studies, some distortions of the pore channels occur during the cutting procedure. If a thin lateral partition of residual non-etched mylar exists inside the pore channel, it may be destroyed at the cutting and it will be transparent for 10–30 keV electrons of a microscope at the direct electron current registration.

To overcome this problem, measurements of the membrane gas conductance were performed. The measurements are based on the relation:

$$q = G \Delta P,$$

where q is the throughput, G is conductance and ΔP is the difference between the pressures at the opposite sides of the membrane.

The measurements of the G value for the regular membranes were carried out using the experimental equipment described in Ref. [5] and they included two evacuated vessels separated from each other by the membrane under examination. The membrane was placed on a teflon support and was sealed along the perimeter by a rubber O-ring and a teflon ring of 25 mm in diameter. Clean air passed from an atmosphere through a primary calibrated hole into the first vessel, came through the membrane and was then evacuated from the second vessel by the rotary vacuum pump. A gas pressure in the first vessel was provided up to 300 Pa and about 70 Pa in the second vessel. The gas pressures in the vessels were measured by a thermoemission current gauge. The gas conductance of the primary hole was found in special preliminary experiments that gives the resulting throughput q and allows one to determine the G value for the membrane. The estimated accuracy for the absolute G value measurements of the membrane is about 15% and is determined mainly by the calibration accuracy of the primary hole.

The pore in the membrane looks like a tube with a pore diameter D and a length L equal to the film thickness. Under the pressures mentioned above, the mean free path of the molecules exceeds 20 μm, which is essentially longer than the pore diameter and the membrane thickness. Therefore, the laws for the molecular gas flow can be applied with a good approximation for the gas conductance calculations. At these conditions, the G value is given by the Knudsen formula [6]:

$$G = 12.1 \alpha D^3 / L, \quad (1)$$

where the Clausing correction factor α can be approximated by the expression [6]:

$$\alpha = (15w + 12w^2)/(20 + 38w + 12w^2)$$

and $w = L/D$. Using the last formulae, G values of 0.11, 0.098 and 0.055 l/s were calculated for 2.5, 3 and 6 μm thick membranes, respectively, assuming a variance of the pore diameters from 0.35 to 0.5 μm over the working area.

Gas conductance values for 3 μm and 6 μm thick membranes were measured. The dependences of the membrane gas conductance upon the etching time are shown in Fig. 3; experimental data for three samples of 3 μm thick and seven samples of 6 μm thick membranes were used to depict this dependence. The diameter of the pores is in proportion to the etching time, therefore the curves, in accordance with the formula (1), describe the experimental results well. It is also clearly seen in Fig. 3 that there is a high spread of experimental G values obtained for different membrane samples. This spread indicates some instabilities in the membrane manufacturing process.

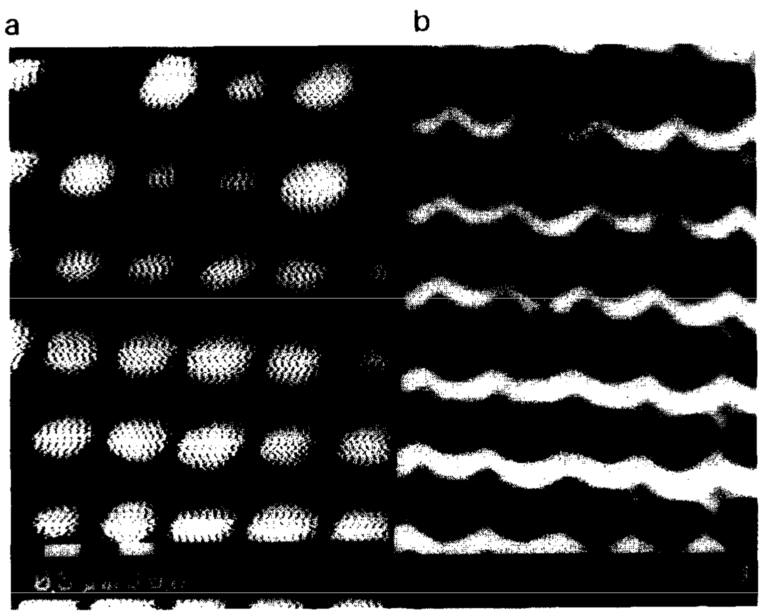

Fig. 2. SEM photographs of the 10 μm thick regular membrane obtained simultaneously by registration of the electron current after the specimen (a) and by conventional registration of the secondary scattered electrons (b).

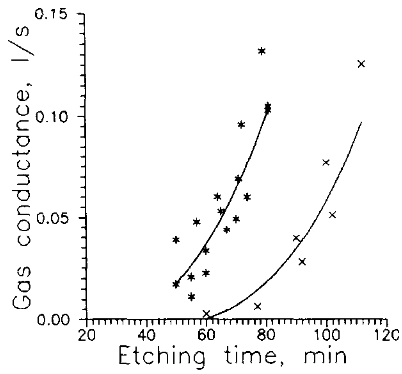

Fig. 3. The dependences of the membrane gas conductance upon the etching time. Experimental data for three samples of 3 μm thick (∗) and seven samples of 6 μm thick (×) membranes are shown.

For comparison, the G value for a 10 μm thick Nuclepore filter [7] with an average pore size of 0.3 μm and with a geometric transparency of about 7.5% was also measured. For the same working area as for the regular membranes, the value 0.036 l/s is determined, while the calculated value is 0.030 l/s. The discrepancy at the level of about 20% may be caused both by a non-accounted for systematic error in the measurements and by the accuracy of the used Clausing approximation in the calculations.

No special investigations of the membrane mechanical properties have been performed but it was found that a 3 μm thick membrane with a diameter of 25 mm is capable to withstand a pressure difference of 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.

The technique of gas conductance measurements proved to be a useful approach for a nondestructive inspection of the membrane integral properties.

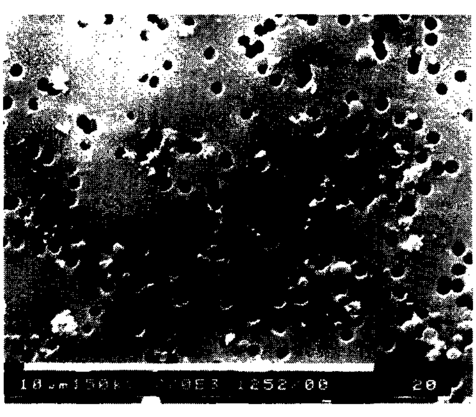

Fig. 4. A SEM photograph of a NUCLEPORE filter based on 8.5 μm thick film with a 0.4 μm average size of the pores.

4. Conclusions

The first experience in manufacturing prototypes of regular microporous membranes shows that the existing technology allows one to produce membranes with submicrometer pore sizes and with a 50% or higher transparency. The shape of the pores can be different from circles; for example, the pores can have a slit or a more complicated form. In contrast to the traditional track membranes having a random locations of pores [7] (Fig. 4), the described membranes have no defects occurring through a confluence of several adjoining pores. The last defects usually limit the transparency of track membranes up to the level of about 10%. Besides that, the regular membranes can have a very uniform pore size distribution, which is important in some applications.

The level of technology of X-ray mask fabrication, which we have in our hands at present, allows us to manufacture masks with a minimal size of the elements (as small as 0.25 μm) over the working area of 25 × 10 mm^2 [8]. It means that regular membranes with the same minimum pore size can be manufactured, and that the working area of the membranes can be increased to up to 25 × 40 mm^2 by a multiplication procedure. Some approaches for manufacturing the X-ray masks with pattern elements of down to 0.1 μm are seen but experimental verification of these possibilities is needed. It seems also that some other polymer materials, different from mylar, can be used for membrane manufacturing.

The first results also indicate that some efforts should be undertaken to improve the quality of the manufactured membranes and to refine the technology processes to obtain quite stable membrane parameters.

Practically simultaneously with manufacturing, the membrane testing for applications in different fields has started to reveal its advantages and disadvantages. So, the membranes were applied, as filters, for precipitating atmospheric aerosols and suspensions in liquids followed by further SR X-ray fluorescent analysis for element contents [9]. The obtained results are about the same as with the use of Nucleopore track membranes. This means that the regular membranes can work as normal filters, and their employment for X-ray fluorescent elemental analysis allows us to hope for an increased effect-to-background ratio due to both the increased amount of analyzed collected substance and the decreased mass of the substance membrane backing, when the membrane transparency will be increased.

The investigations of the membrane selective properties for microparticles and bacteria cells have shown the high capabilities of the membranes for application in low temperature sterilization of liquids, as well as the possibility of using them as standard reference membranes for certification of different filters and microparticles [10].

Other potential applications of the membranes are under consideration at present.

Acknowledgements

The authors thank V. Golynsky and V. Vasilenko for their technical assistance, and E. Yakovleva for specimens treatment. Also they thank Dr. V. Baryshev and Dr. B. Mchedlishvili for their constant interest and for the comparison of the regular membranes with the usual ones in the field of X-ray fluorescent analysis and testing the selective properties of these membranes.

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