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ABSTRACT

The X-ray lithography with synchrotron radiation at the VEPP-3 storage ring was applied for fabrication of polymer microstructures with submicron 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 fabricated 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 different techniques are presented. Possible improvements of the membrane parameters and some potential applications of the membranes are discussed as well.

Key words: X-ray lithography, regular microporous membranes, synchrotron radiation, high aspect ratio microstructure.

1. INTRODUCTION

X-ray lithography has made steady progress in the last decade because of its intrinsic high-resolution capability. Now it becomes to be applied for fabrication of high aspect ratio micromechanical devices with a few μm elements which are beyond of the practical fabrication limits of optical lithography and dry

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etching techniques. In a technological sense, this x-ray process with the use of synchrotron radiation (SR) is a part of the LIGA technology [1]. The high intensity and high collimated SR beams allows one also to manufacture the regular track membranes (RTM) with the submicron pores.

The usual track membranes (TM) are produced by heavy ions and fission nuclear fragments irradiation of polymer films. The ions cause changes in polymer molecules of a film, and a postirradiated treatment of the film produces holes at the locations of ion tracks. The track membranes mentioned above are known as Nuclepore filters [2]. A porosity of the TM usually is not higher than 10-20 % because the increase of pore density leads to the merging of adjoining pores and to the deterioration of the membrane selectivity properties. As for the RTM, the merging of adjoining pores is eliminated by the regular arranging of pore locations therefore a porosity can be obtained of up to 50 % and higher.

This paper describes some details of fabrication of the submicron pore size RTM and investigation of their properties. Possible RTM applications are discussed as well.

2. FABRICATION CONCEPT

2.1. X-ray mask

The mask fabrication procedure was previously reported [3]. In the present work, we have used E-beam writer ZBA-20 (Karl Zeiss firm) for the microlithography manufacture of eight arrays of microholes. Every array was composed of squares of 200×200 μm with the holes and with the free holes strips between the squares. The holes were written in a resist layer of every square with a 1 μm period in two directions. A diameter of the holes was designed with a change from a 0.5 μm in the first array to a 0.35 μm in the eighth array with a precision of a 0.05 μm. A porous area of the X-ray mask is 25×1.6 mm^2.

The X-ray mask was fabricated on the base of boron doped silicon wafer. The titan and nickel films were evaporated onto the wafer as a background for the gold electroplating. To create the holes in the gold absorbing layer, the regular SiO_2 columns of a 1 μm high and of a 0.35-0.5 μm diameter were originally formed. Then, the electroplating of a 1 μm thick Au film was carried out and the SiO_2 columns were removed by dry etching. To increase the X-ray mask contrast, Ti and Ni films were etched as well. Then, the silicon wafer was etched from its back side till the etching stops and the silicon membrane of a 2 μm thick forms.

Inspection of the Au film of the X-ray mask revealed a limited number of puncture defects (large inadmissible porous) in the RTM. These defects were repaired by rhenium using the LCVD method [4]. The integral contrast of the X-ray mask is about 23 for the X-ray spectra of the lithography station of the VEPP-3 storage ring [5].

2.2. Investigation of the X-ray interaction with mylar film

Many kinds of films were used for the TM fabrication [6-8], and mylar (polyethyleneterephthalate) films are one of the typical material [9,10]. In the case when the mylar film interacts with ions, the processes of the destruction and joining of molecules occur simultaneously [8]. The main reason of increase of the etching rate of mylar film in the ion track areas is the formation of large number of end carboxylic groups due to the destruction of molecules. The radiochemical yield G of carboxylic groups was 0.62 /100 eV under irradiation of mylar film by Xe ions, and the linear energy transfer (LET) was 10^4 eV/nm [8]. For gamma-irradiation of mylar film with the LET of about 0.2 eV/nm, the G value lies in the range from 0.6 to 0.77 per 100 eV [8]. In our case the LET value integrated over the absorption spectrum is 0.08 eV/nm, and one could expect that

G value is close to the one mentioned above.

It is known that mylar films have amorphous and crystalline phases [11], and the amorphization of mylar films after heavy ion irradiation was found earlier [17]. In our work, the IR spectra of mylar films were analyzed to determine the changes in the films after their X-ray irradiation. The spectrophotometer "Specord M75" for 400-3800 cm^{-1} range was used for this purpose.

The IR spectra of the pristine mylar film and the film irradiated with the dose of a 36 kJ/cm^3 are shown in Fig. 1. This exposure dose exceeds by about 2.5 times the dose required usually for the RTM fabrication. Some changes in the spectra were observed. The absorption at 3256 cm^{-1} and at 3542 cm^{-1} indicating the existence of carboxylic and hydroxyl groups was changed. In addition, the decrease of intensities of the bands at 1387, 1120 and 845 cm^{-1}, and the increase of intensities of the bands at 1370 and 1110 cm^{-1} are observed as well. The observed spectra changes agree with the results obtained by other authors [17]. Such changes of the IR spectra can be interpreted, with the use of the IR-peaks list [11], as the increase of the amorphous part and the decrease of the crystalline part of the phase composition. It is possible to assume that such the phase composition change of mylar film is caused by decrease of molecule-molecule bond energy or/and the change of polymer chain length.

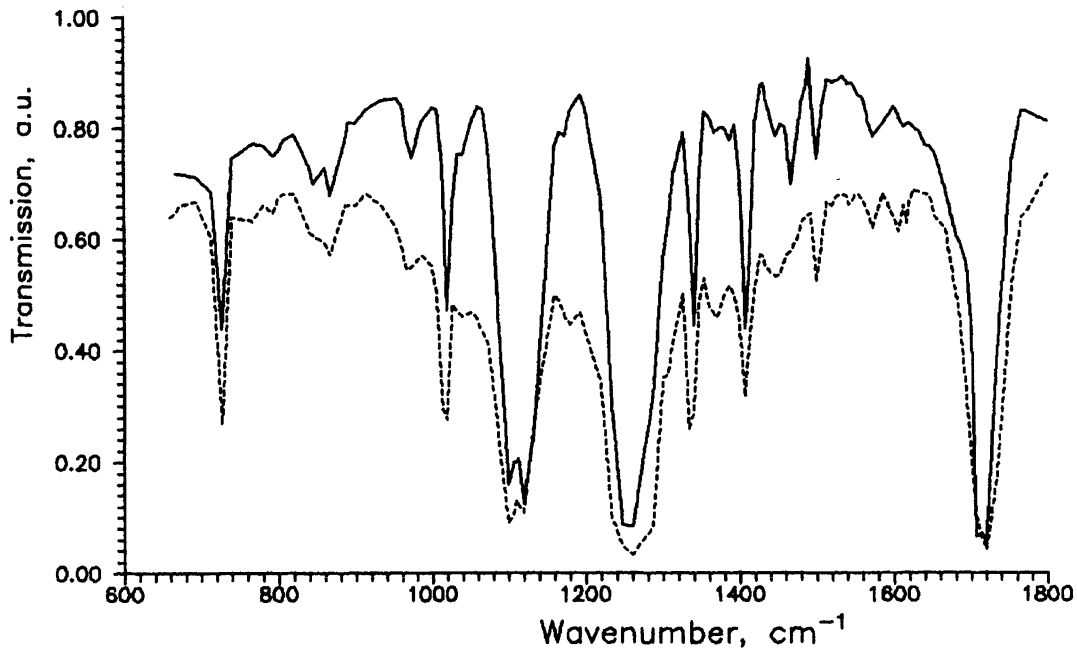


Fig. 1. IR spectra of mylar samples: solid curve - pristine film, dotted curve - the film with a 36 kJ/cm^3 exposure by X-rays.

It has been concluded that the dissolving rate of the mylar film rises after the X-ray irradiation (Fig. 2). A KOH water solution was used as a dissolvent. The curve has a monotonous character which is different from the one for the case of Ar and Cl heavy ions irradiation [10].

Figure 2 clearly shows the response of the dissolving rate versus the X-ray exposure dose. The response starts from about 560 J/cm^3 (400 kGr). However, the response after heavy ions irradiation already reaches a saturation by this dose. Despite of different interaction behavior of X-rays and heavy ions with mylar, the G equivalence for the carboxylic groups allows one to find optimal conditions for the mylar treatment.

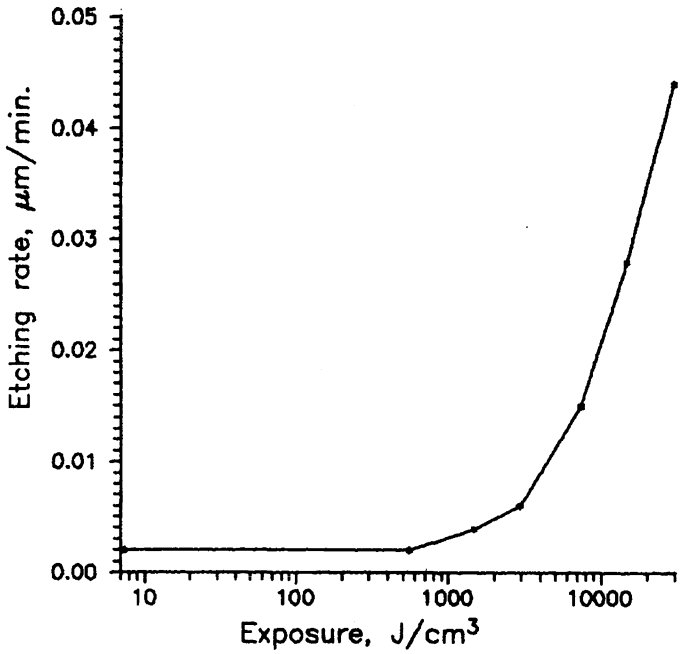


Fig. 2 Dependence of the etching rate of the mylar film on the X-ray dose.

2.3. RTM fabrication

For the RTM fabrication, the mylar films of 2.5, 3, 6, and 10 μm thickness were used. The film and X-ray mask were mounted into a vacuum chamber of the X-ray lithography station at the VEPP-3 storage ring. After evacuation of air, the chamber was filled with helium to a pressure of up to 1000 Pa. The gap between the X-ray mask and the mylar film was set to 30 μm that warrants the absence of diffraction distortions at the level of higher than 0.15 μm. Due to a high penetration of the X-rays under a typical mode of the lithography station operation, it is possible to irradiate also a pile of mylar films with a total thickness of up to 20 μm.

The exposed films were etched in an alkali solution for about a 1 hour, then rinsed in water and dried by clean air. An additional UV irradiation of the exposed films was tested as well but no any significant influence on the etching rate was observed. The SEM photographs of the fabricated RTM as well as commercial TM are shown in Fig.3. To increase the working area of the film, in some cases the x-ray mask pattern was multiplicated into the film by the station stepper (see Fig.4).

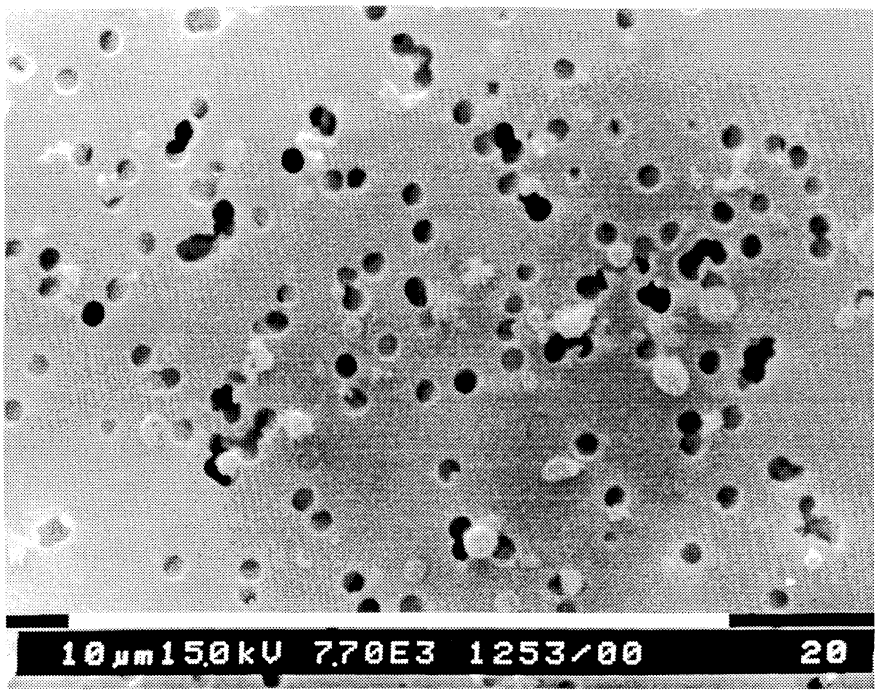
3. RTM TESTING

The pore size distribution of fabricated RTM was investigated by extrusion of latex and corundum microspheres of 0.2-1 μm diameter through the holes of the RTM [15]. The measurements confirmed that the RTM through pores have a small value of pore diameter spread.

The membrane microstructures were examined also by a scanning electron microscope (SEM). As can be seen in Fig.3, the pores have a cylindrical shape with their cross sections being close to circles. The walls of the pores are rather smooth and a lamination of the film is not occurred. The SEM measurements have shown that the average diameter of the pores of the RTM is close to the one on the X-ray mask pattern. To

obtain this result for a 3 μm thick film, the etching time of about an hour is required. Further etching leads to the increase of the pore diameters and to the merging of neighboring pores.

a)



b)

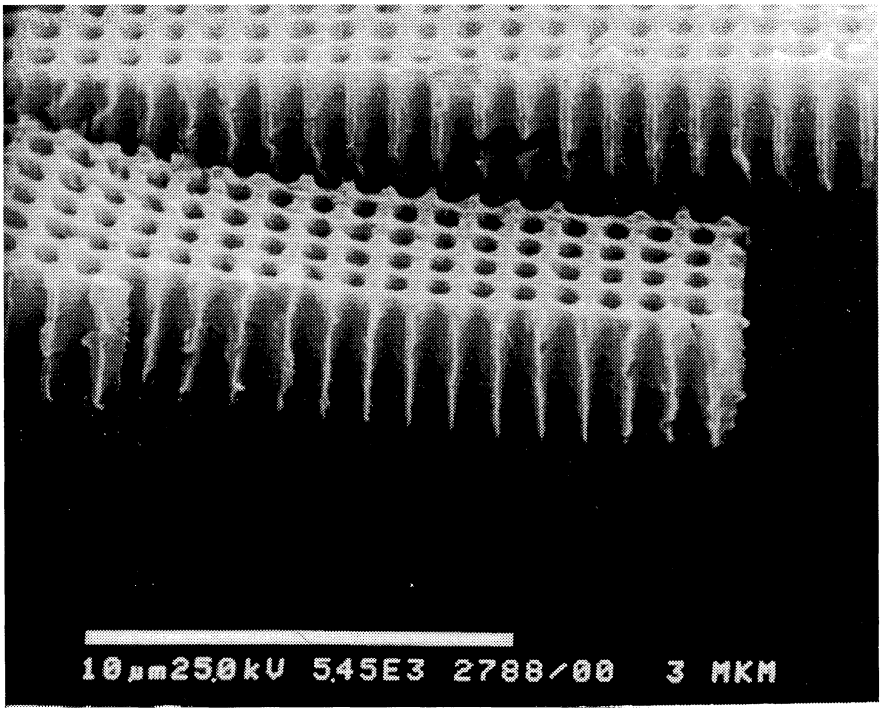


Fig.3. SEM photographs of the filters: a) a Nuclepore filter; b) cross section of the 3 μm thick RTM.

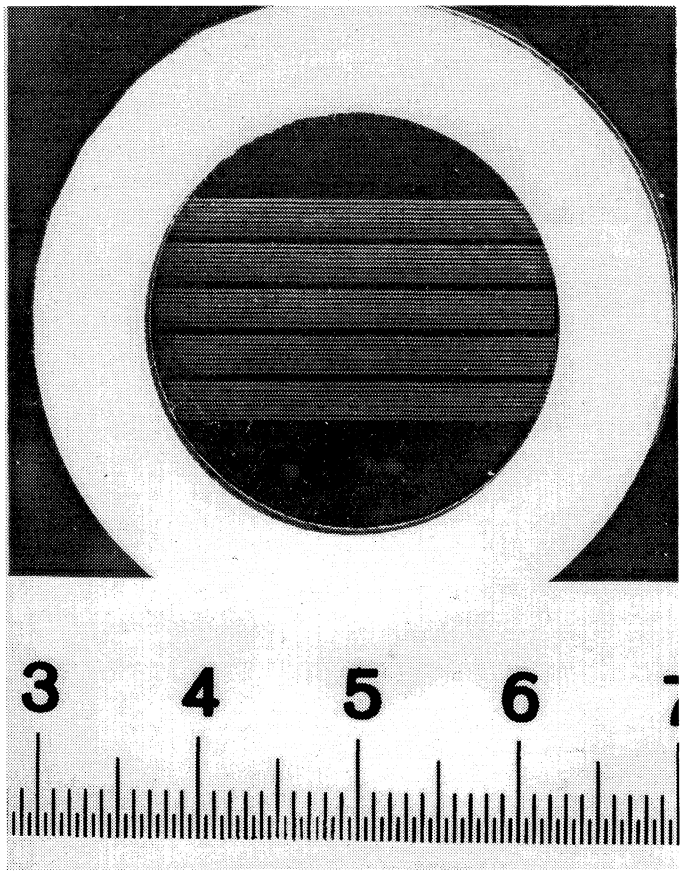


Fig.4. General view of the RTM with a 5-fold pattern multiplication.

The through pores were observed also by SEM in a transmitted e-beam mode [12]. The image in this mode repeated and confirmed the circle shape of the pores. However, this method does not give an absolute guarantee in existence of through pores because, for example, a thin cross piece inside of the pore is transparent to the 10-30 keV electrons. To be sure in existence of through pores, the method of the gas conductance measurements was used as well.

The used equipment was described earlier [13]. The membrane have being set up in a mount between two vacuum spaces. Air was passed through a calibrated hole into the first space, flowed out through the filter to the second space and was exhausted by a vacuum pump. The pressure inside of the both spaces changed in the range from tens to thousands Pa. The conductance g of the RTM was calculated from the expression $g_{exp}=Q/P$, where Q is a throughput, P is a pressure difference measured by vacuum gauges at the opposite sides of the filter. The Q value was measured by a water manometer.

On the one hand, the average diameter of pores was calculated from the measured value of g using the Knudsen expression for molecular flow and the Klausing factor for a short channel [14]. On the other hand, the theoretical value of g_{theor} was expressed on the base of measurements of diameter of some pores by SEM. It was assumed in the calculations that the diameter of pores changes linearly from the first to the eighth array. If the diameter of pores in the first array is equal to a 0.5 μm, g_{theor} becomes equal to g_{exp}. The uncertainty of this equivalence is determined by the measurement errors and expected to be not higher than 15 %. For a 0.5 μm diameter pores, the resulting integral conductance has the value of about 0.075 l/s for

a 3 μm thick membrane, and the 5-fold multiplicated filter has the value of up to 0.37 l/s, correspondingly, that is equally to 0.21 l/s per 1 cm^2 of the porous area. For comparison, the g_{exp} value for the TM of a 8.5 μm thick 0.6 l/s was found, that corresponds to 0.07 l/s per. 1 cm^2 . These difference in the measured values is explained by the difference of the films thickness.

The use of the RTM for filtration of liquids, matter particles and so on, may require other appropriate methods for measuring the RTM penetration capabilities. So, for example, the membrane selective properties were investigated by penetrability of the *Pseudomonas diminuta* bacteria with a 0.3 μm average size [15]. It was shown that all bacteria were retained by the filter with a 0.32 μm average pore diameter.

4. DISCUSSION

The investigations have shown that the X-ray contrast of the mask absorber film and the metal film deposited on the mask by the LCVD is rather enough to exposure organic films of several tens microns deep at the VEPP-3 lithography station. A high spatial resolution at a repairing of an x-ray mask is not very essential but it is required that absolutely all puncture defects on the X-ray mask absorber are repaired to be sure that bacteria or other kinds of particles can not penetrate through the fabricated membranes.

It is seen from Fig. 3 that the membrane porosity can be increased up to about 50 % and higher by specifying the appropriate arranging of the pores on an X-ray mask pattern. RTM can have a larger number of pores per area unit, than the Nuclepore filter with the same pore diameter, it is possible to increase the signal/Compton background ratio for X-ray fluorescence element analysis of extremely small amounts of elements using the RTM. Preliminary investigations of the RTM as filters for collection of aerosols particles and water suspensions for further X-ray fluorescence analysis were carried out [16].

Due to aforementioned valuable properties and chemical resistance of the RTM, they can be used in biotechnology, microbiology, pharmacology, and medicine. For instance, the membranes can find employment for separation of blood cells, air sterilization at 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.

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

The RTM fabrication method does not eliminate the use of other kinds of polymer films for special purposes by choosing the appropriate technological process of the film treatment.

5. CONCLUSION

This work demonstrates our successful application of the first step of LIGA technology, deep X-ray lithography, for manufacturing non-microelectronics microstructures with submicron sizes of elements and with rather high aspect ratio. The offered microstructures may have new valuable properties and can find many interesting applications due to their intrinsic properties.

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