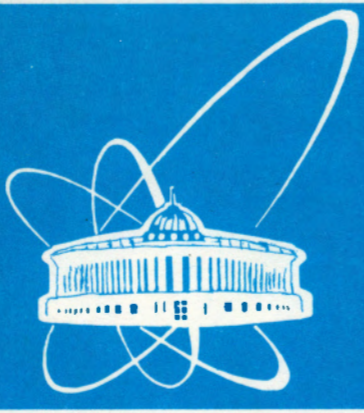

СООБЩЕНИЯ
ОБЪЕДИНЕННОГО
ИНСТИТУТА
ЯДЕРНЫХ
ИССЛЕДОВАНИЙ

Дубна

E18-98-367

V.F.Reutov, S.N.Dmitriev, A.S.Sokhatsky, G.N.Akapiev

TRANSMISSION ELECTRON MICROSCOPY POROMETRY OF TRACK MEMBRANES

1998

Introduction

Track Membranes (TM) have found wide use in many fields of science and industry [1]. Further progress in their use depends on development of the technology of controlled change in the etch (geometric) profile of the pores, especially those of nanometric size. In this context the problem of porometry, especially the analysis of the etch profile of nanometric pores at the immediate subsurface layer of the TM is actual.

Among all existing indirect methods of TM porometry, Scanning (SEM) and Transmission Electron Microscopy (TEM) provide conditions for the direct observation of the etched channels in TM, and therefore permit the measurement of their diameter and its variation throught the TM thickness (i.e. the geometric profile of the pore channel).

SEM allows direct observation of pore diameter on the TM surface as well as, , of their geometric profile throughout the TM thickness by fracturing the TM. However, the limited SEM resolution and the residual deformation of the TM resulting even if freeze fracture is employed, severely limits the quantitative information that can be obtained about the parameters of pore channels of nanometric size (< 100 nm).

The direct observation of pore channels with TEM requires cutting ultrathin layers from the TM on a ultramicrotome. This substantially lengthy and laborious method also results in non-negligible distortion of the dimensions and geometric pore profile due to the significant deformation resulting from the process of cutting.

There is therefore a need for a method for the preparation of a unified sample with parameters suitable simultaneously for both SEM and TEM, and providing the conditions for the measurement of the actual sizes and geometric pore profiles, in a wide range of pore diameters from 15 nm and above.

A method for the preparation of such a unified SEM/TEM sample would center around the process of electrochemical deposition in the TM pore channels of an appropriate metal, usually copper, and the creation of a Metallic Replica (MR) of the pore channels [2].

The process of formation of a MR in the TM pore channels consists of two stages which define the quality of the resulting sample: first, the nucleation of the MR and second the growth of the MR. The success of the nucleation stage depends on the quality of the contact of the TM with the cathode electrode and the wettability of the internal volume of the pore channel, especially given its nanometric size.

The MR growth stage is governed by the consistence and temperature of the electrolyte, the current density, as well as by the density of the etched tracks in the TM, the area of the track cross section and its variation along the TM thickness.

Finally, the method of preparation of unified MR samples for SEM/TEM TM porometry must be simple, easily controllable and as fast as possible.

A necessary condition for the growth of MR is the creation of a metallic precipitate in the TM pores. To this end, on one of the TM surfaces, a thin (0.05 - 0.1 mm) metal layer which serves as a cathode is formed by vacuum deposition. Following that the pore channels are filled with metal by electrochemical deposition in a special electrochemical cell with appropriate electrodes. In this process, the conditions of the electrochemical deposition (potential, current density, temperature) are chosen so as to obtain a monocrystalline metal structure in the resulting deposition. The MR growth process is completed when the precipitate reaches the opposite side of the TM. After the completion of the MR growth process, a massive metal substrate (thickness of 10 to 20 mm) is formed either by continuing the electrochemical deposition on the exit side of the TM or by the electrolytic deposition of metal on the initial, sputtered side [2]. Next, the MR is isolated from the TM by etching away the TM matrix in a caustic solution. A washed out and dried MR can then be observed under SEM.

Note that SEM analysis of MR is generally used for TM with pore sizes larger than 0.1 mm. For nanometric pores (less than 0.1 mm) TEM is used which has higher resolution than SEM. To that end, after etching away the TM matrix, a small MR piece is broken off and is fished out from the solution in a special supporting mesh which is then loaded in the TEM for observation.

The disadvantages of the above described method are:

- The use of vacuum deposition of a metal layer on one side of the TM, which not only significantly increases the time of sample preparation but it also distorts the pore channel profile near the TM surface from which

starts the MR formation process, since it introduces metal on the internal pore surface.
- The non-sufficient mechanical strength of the coupling between the MR and the supporting massive metal substrate (especially for TM of nanometric pore sizes).
- Because of the residual stress in the electrochemically deposited metal substrate, it deforms (twists) and further complicates the handling of the sample for TEM analysis.
- Difficulty of breaking off and, together with the main piece, extracting from the solution on the supporting mesh additional MR which results in contamination of the TEM column.

A new method of sample preparation for porometry of TM pores with any etch profile larger than 10 nm, appropriate for both SEM and TEM microscopy, has been developed at JINR (CAP of FLNR). The Metallic Replicas (MR) are formed directly on a pre-existing massive substrate (copper foil), so as to completely avoid all aforementioned disadvantages of MR formation with the metal sputtering of TM.

Results

Polyetheleneterephthalate (PETF) films of 10 mm thickness, irradiated with 210 Mev Krypton ions at the U-400 cyclotron (JINR, Dubna), were used as TM samples. Ion flux was between 10^8 and 3×10^9 cm^{-2}. The samples were irradiated with UV light and subsequently etched in 6N NaOH solution at 60° C for various lengths of time depending on the required pore diameter. Various pore etch profiles across the width of the film were obtained with the use of surfactants as well as with the use of gas discharge etching.

In the new method, the electrochemical deposition of copper in the TM pores takes place in a $CuSO_4 \cdot 5H_2O$ (70 g/l) + H_2SO_4 (175 g/l) + H_2O (added to 1 l total) in a galvanostatis regime at room temperature. The current density, because of the inability to define the surface area of the copper deposition, is not controlled. The electrode potential is selected empirically so as to achieve a good quality of deposition (the deposition structure must be monocrystalline copper), and is set between 0.25 and 0.4 Volts. The termination of the process of copper deposition throughout the TM thickness (i.e. throughout the pores length) is controlled with the help of an optical microscope, upon detection of deposition beyond the end of the pore channels as indicated by the formation of the characteristic

"mushroom-like" growths. Total deposition time is between 10 and 15 minutes.

A copper foil of 50 mm is used as a massive substrate on which the MR are grown. It is initially electropolished to a "shining mirror" level. Following that, 3 mm disks are cut out, corresponding to the size of the TEM sample holder. Note that this sample size is also appropriate for SEM analysis.

By impressing a metal ball on the disks, spherically shaped profiles are obtained. A thus spherically shaped disk is then mounted on the surface of a specially prepared electrochemical cell. The TM is laid on the disk and is fastened down between the donut shaped anode electrode and the base of the electrochemical cell, as shown in Fig. 1. A vacuum is then introduced between the disk and the TM surface, clamping down the TM on the spherical disk surface. At the same time the disk is pressed against the cathode electrode maintaining a reliable electrical contact with it. Electrolyte is then added to the cell for the electrochemical deposition in the TM pores.

After the completion of the deposition, which is reached when the characteristic "mushroom" growths are detected with an optical microscope, the electrolyte is emptied from the cell and the cell is washed with water.

The separation of the MR from the TM is effected by etching out the TM matrix with a caustic solution which is added to the electrolytic cell. For PET TM, a 6 N NaOH solution at 80°C is used. Within 5 to 7 minutes, after complete etching of the TM matrix, the MR is extracted and washed with running water for 2 to 3 minutes.

For TEM examination the disk is bent by 180° degrees around any diameter to obtain a perpendicular direction of the metallic "tabs" with respect to the electron beam in the microscope.

Figures 2 show the results of TEM observations of MR from TM exhibiting various sizes and geometric etch profiles.

TEM investigations have shown that the copper deposited inside the TM pores has practically monocrystalline structure, which, in combination with its good coupling to the massive metallic substrate, allows the MR to withstand strong mechanical stress - i.e. 180° degrees bending of the MR disk with the MR.

Note that this method of MR formation on a massive substrate allows the efficient production of high quality samples for SEM study of the geometric profile of pore channels of micron and submicron size, without

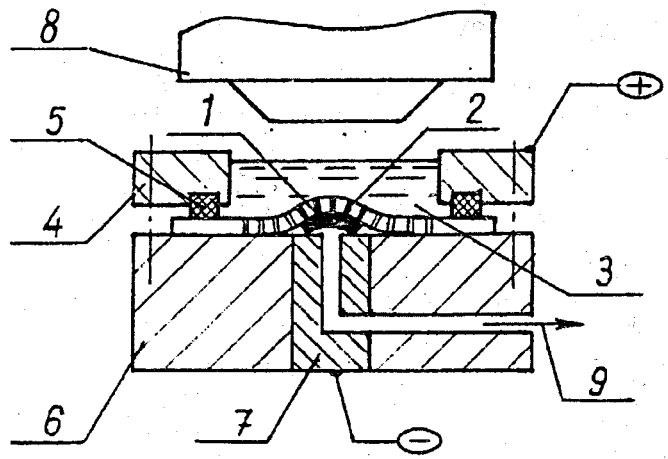

Fig. 1. Schematic diagram of the setup used to produce MR from TM.
1 - massive substrate (copper foil of 50 mm thickness), 2 - Track Membrane, 3 - electrolyte, 4 - anode electrode, 5 - gasket, 6 - main setup body, 7 - cathode electrode, 8 - optical microscope, 9 - vacuum line

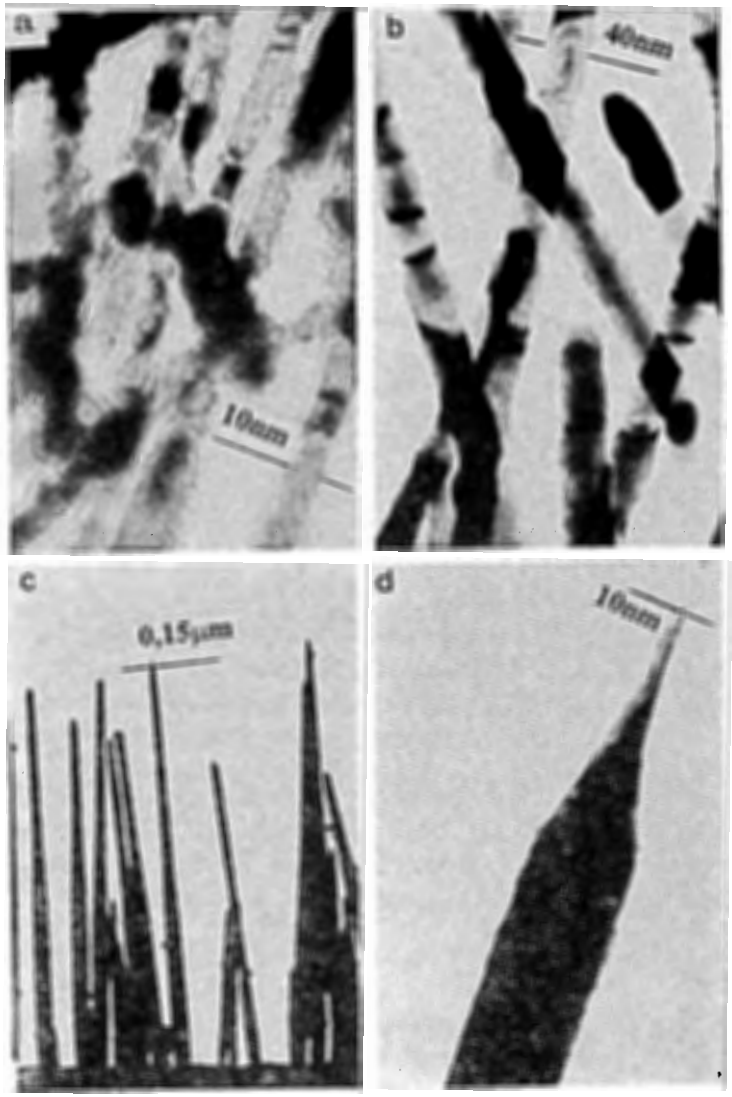

Fig.2. TEM-images of metallic replics with various etch profiles pores:
a,b - cylindrical pores,
c - conical shaped pore,
d - "bottle" shaped pore

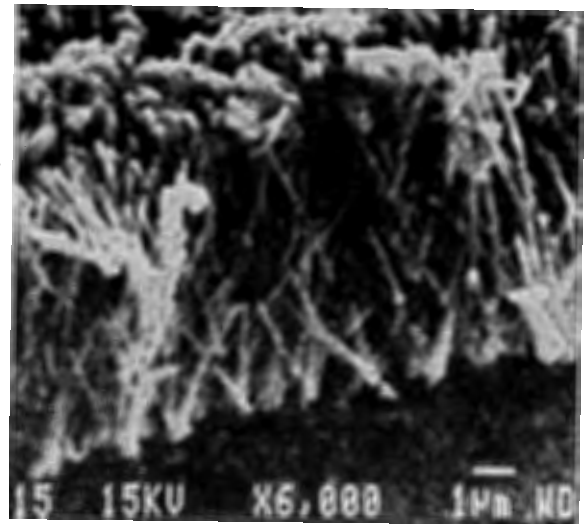

Fig. 3. SEM images from metallic replics from track membrans.

the distortions of shape and size possible when fructure methods are used to produce samples (Fig.3).

This way, the application of the suggested method allows a quick and reliable sample preparation for both SEM and TEM observation which is very important for quality control of a production setup of TM with requirements for specific diameters and pore profiles, especially of nanometric dimensions. The total time required for the preparation of the unified SEM/TEM samples with the previously used method, which utilized vacuum deposition of a metallic layer on the TM and a subsequent electrolytic deposition of a massive substrate, was no less than 8 to 10 hours.

Conclusion

A fast method has been developed for the preparation of a sample appropriate for both SEM and TEM porometry of Track Membranes with pore-channels of various geometric profiles and of size 10 nm and above.

The method leads to the electrochemical deposition in the pore channels of a precipitate of monocrystalline copper directly on the surface of a copper foil disk bent into a spherical shape. The tight clamping of the Track Membrane on the disk surface is carried out by the creation of a vacuum in the space between them.

1. G.N. Flerov. Cintez sverkhtyajelikh elementov i primenenie metodov yadernoy phiziki v smejnikh oblastyakh. Vestnik AN SSSR. 4(1984) 35-48.

2. S.V.Vetter, R.Spohr. Application of ion track membranes for preparation of metallic microstructures. Nucl.Instr. and Meth. in Phisics Research. B79 (1993) 691-694

Received by Publishing Department
on December 21, 1998.

Реутов В.Ф. и др.
E18-98-367

Порометрия трековых мембран с помощью просвечивающей электронной микроскопии

Описан экспрессный способ приготовления унифицированного объекта для РЭМ\ПЭМ-порометрии трековых мембран с каналами различного геометрического профиля и размерами 10 нм и более.

Способ заключается в гальваническом осаждении в каналах осадка в виде монокристаллической меди непосредственно на сферически изогнутую поверхность диска из медной фольги. При этом плотное прижатие трековой мембраны к поверхности диска осуществляется созданием вакуума в пространстве между ними.

Работа выполнена в Лаборатории ядерных реакций им. Г.Н.Флерова ОИЯИ.

Сообщение Объединенного института ядерных исследований. Дубна, 1998

Reutov V.F. et al.
E18-98-367

Transmission Electron Microscopy Porometry of Track Membranes

A fast method has been developed for the preparation of a sample appropriate for both SEM and TEM porometry of track membranes with pore channels of various geometric profiles and of size 10 nm and above.

The method leads to the electrochemical deposition in the pore channels of a precipitate of monocrystalline copper directly on the surface of a copper foil disk bent into a spherical shape. The tight clamping of the track membrane on the disk surface is carried out by the creation of a vacuum in the space between them.

The investigation has been performed at the Flerov Laboratory of Nuclear Reactions, JINR.

Communication of the Joint Institute for Nuclear Research. Dubna, 1998