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Fabrication of metallic and polymeric microstructures using ion track filters

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Fabrication of microstructure is being considered a potential technology not only for use in microelectronics and micromechanics but also in the studies pertaining to behaviour of materials at nano or microscopic scale. The synthesis of microstructures and microtubles of desired material, viz., metal, polymer and metal-semiconductor within the etched pores of Makrofol-KG, kapton and PVDF has been described. The developed microstructures and replicas were scanned by SEM for morphological studies.

1 Introduction

Microtechnology relies essentially on the generation of replicas (metallic or non-metallic), for example, in the field of micromechanics[1,2]. A variety of possible applications include high power microwave generation, ultrafast computer and terahertz amplifier devices fabrication, radiation and temperature insensitive electronics[3-5]. Development of metallic microstructures comprising either metallic microdimensional devices, dots, fibers, wires, cones, tubules and whiskers have provided exciting applications in multidisciplinary fields such as microelectromechanics[6], field ion emitters/electrodes[7], materials science and microtechnology[8], biological substitute for microtubules[9], single volcano field emitters[10]. The latest developments in this field are semiconductor nanometer whiskers[11], nanotubules[12,13], crystalline microstructures[14], magnetic multilayered nanowires[15] etc.. Wu and Bein[16] using a similar approach have also reported solid nanocarbon tubules (graphitic) within the pore of nanoporous xeolite.

2 Materials and Methods

A membrane in general may act as a barrier to the flow of matter. For synthesizing microstructures mostly two types of membranes are used:

(a) Track-etched membranes, also known as ion track filters (ITFs) and (b) porous alumina.

Ion track filters (ITFs) are produced by physicochemical treatments to thin films of polymers and mica irradiated by heavy ions. The chemical etching of irradiated films leads to the formation of fine hollow channels along the path of the charged particles due to preferential etching along the latent trail. If the thickness of the sheet is less than the particle range in it, the above process leads to the formation of the fine pores in the irradiated sheet. The porosity of these membranes can be controlled by the flux of the ion beam and pore diameter can be controlled by ion characteristics and etching parameters like etching time, etching temperature and etchant concentration etc.[17,18]. Porous alumina is prepared electrochemically from aluminium[19] can have high porosity (pore density as high as 10^{11} pores/cm^2), pores are arranged in hexagonal array but commercially available in only a very limited values of pore size.

In the present paper, ITFs of Makrofol-KG and Kapton have been used for synthesis of microstructures. The replication of heavy ion pores in PVDF is also reported in this study. The details of materials used, heavy ion beams, etching conditions and pore diameters are summarized in Table 1. The techniques used for the development of microstructures and replications of heavy ion pores in polymers are given as follows:

2.1 Template synthesis of metallic copper (Cu)

The methodology of the development of microstructures using this technique is based upon the earlier work of Possin[20], Williams and Giordano[21], Penner and Martin[22] and Chakravarti and Vetter[23] producing thin metal

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Table 1 — Detailed specification of the ITFs used for generation of microstructures

Material	Thickness (μm)	Irradiation*	Etching conditions	Average pore diameter (μm)	Pore density (per cm^2)
Makrofol-KG (Bayer AG)	90	^{238}U(13.6 MeV/n)	6N NaOH 70°C	3.3	10^6
Kapton-H	100	^{238}U(13.6 MeV/n)	NaOCl(13% Cl) 60°C	1.5	10^6
Polyvinylidene fluoride (PVDF)	50	^{238}U(11.6 MeV/n)	$KOH+KMnO_4$	10.0	10^4

*Irradiations were carried out at UNILAC, GSI, Darmstadt, Germany

wires. The simplest and well known underlying concept of electrodeposition of metals through electroplating is described as an electrochemical process. The basic setup of this technique is given in Fig. 1. The metallic ions in a supporting solution have been reduced to the metallic state at the cathode which was closely covered by an ITF, would lead to the formation of growth of plated film as an embodiment of micro-structure. The etched pores of ITFs used would act as a template. The electrolyte used here was $CuSO_4.5H_2O$ acidic solution in distilled water. The rate of deposition of metallic film depends upon many factors, i.e., current density, inter- electrode distance, cell voltage, electrolyte concentration and flow conditions, temperature etc. In the present setup inter-electrode distance was kept at 0.5cm and an electrolyte with a composition of 20gm/100ml $CuSO_4.5H_2O$ + 25% of dil. H_2SO_4 at room temperature (33°C) was used. A current of 0.0025 (A) was applied for 50 min. for Makrofol-KG and 1hr for kapton. This value of optimum current i(in amps) calculated by using the method and relation given by Chakravarti and Vetter[23].

After the electrodeposition was over, the electrolyte was drained out and the copper electrode was detached from the copper substrate. The chloroform ($CHCl_3$) was used as a solvent for dissolution of ITF film of Makrofol-KG followed by rinsing with water and ethanol. The developed microstructures were scanned under scanning electron microscope (SEM) (Jeol, JSM-6100) for morphological and structural studies.

2.2 Template synthesis of polymeric fibrils (plastic replication)

Track replication is considered to be one of the appropriate methods for evaluating the significant track parameters which otherwise are not possible to be obtained through use of SEM-a very potent and mandatory device in such investigations but suffering from the limitation that it can peep through the track channels up to a few microns[24]. It may be interesting to note that the fabrication of conductive polymeric fibrils is also based upon the important consideration that enhanced electronic conductivities are obtained if polymers acquire enhanced molecular (comprising fewer conjugation-interrupting defect sites) and supermolecular order, hav-

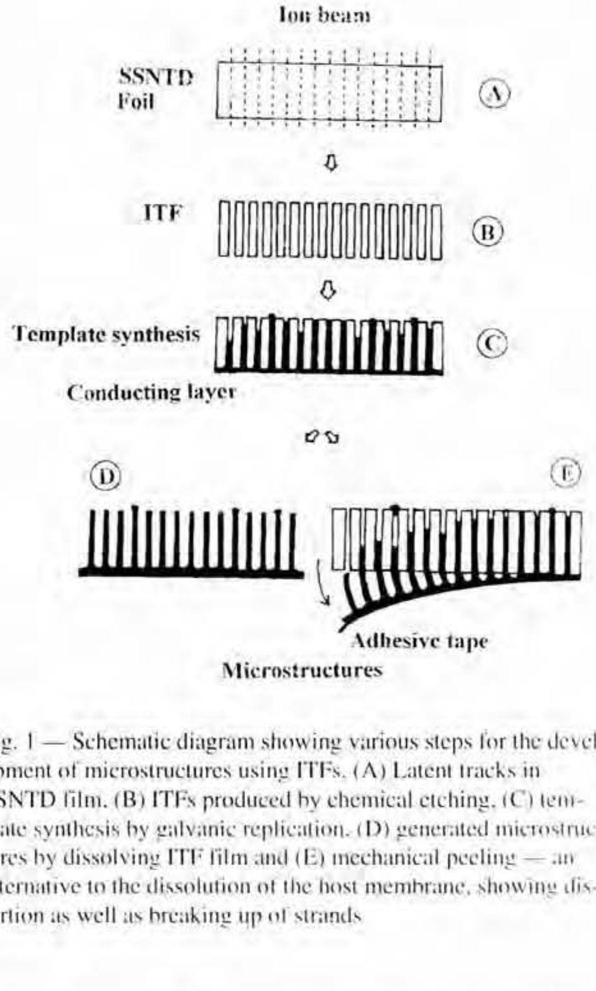

Fig. 1 — Schematic diagram showing various steps for the development of microstructures using ITFs, (A) Latent tracks in SSNTD film, (B) ITFs produced by chemical etching, (C) template synthesis by galvanic replication, (D) generated microstructures by dissolving ITF film and (E) mechanical peeling — an alternative to the dissolution of the host membrane, showing distortion as well as breaking up of strands

ing ordered polymeric chains through stretching and crystallization. These can be synthesized by oxidative polymerization of the corresponding monomer which can be accomplished either electrochemically or by using chemical oxidising agent. A simple method which can be used for production of polymeric solid fibrils-Micro Grass is to dissolve the given polymer in an organic solvent and permit to settle down this viscous fluid through the membrane. After it gets dried up, the microstructure is pulled up using an adhesive tape. This technique has been used while resorting to the replication of the pores, which may yield distorted replica resembling Micro Grass[23].

In this paper, the replication of etched pores in PVDF ion track filters has been reported. For this purpose, Makrofol-KG film was dissolved in $CHCl_3$ and the solution was spread over the flat and cleaned surface of the ITFs. After drying, the thin film was carefully peeled off from the ITF using adhesive tape. The replicas were coated by sputtering gold on it and scanned under SEM.

3 Results and Discussion

Fig. 2 shows that the prolonged metal deposition may lead to gradually emerging metal buds on top of the membrane. Fig. 3 and 4 show the pins produced from multipore ITFs of Makrofol-KG having thickness of 90µm. Fig.4 shows smoother pins than in Fig. 3. This is due to the fact that in the former case the metal deposition was prolonged as compared to the latter case. An isolated pin grown through the ITFs of Makrofol-KG is shown in Fig. 5.

Fig. 6 shows the top view of pins matrix produced from kapton sample of thickness 100µm and having a pore diameter 1.5 m with a pore density $10^6/cm^2$. Kapton is a polyimide with exceptional qualities like high chemical resistance, excellent thermal stability and good mechanical strength. This material is currently of much interest for its use as ITFs. Fig.7 shows the grown replica of ^{238}U (11.6 MeV/u) ion pores in polyvinylidine fluoride(PVDF) having thickness 50 µm. The apparent formation of hollow polymeric tubules is not well understood. One possible reason could be that the pore walls in PVDF may be charged leading to the layered deposition of the replicating fluid containing Makrofol, a polycarbonate which is polar.

Taking into consideration the simplicity of the technique involved, the use of ITFs looks quite promising in the fabrication of microstructures. The morphology study of such structures produced through electrochemi-

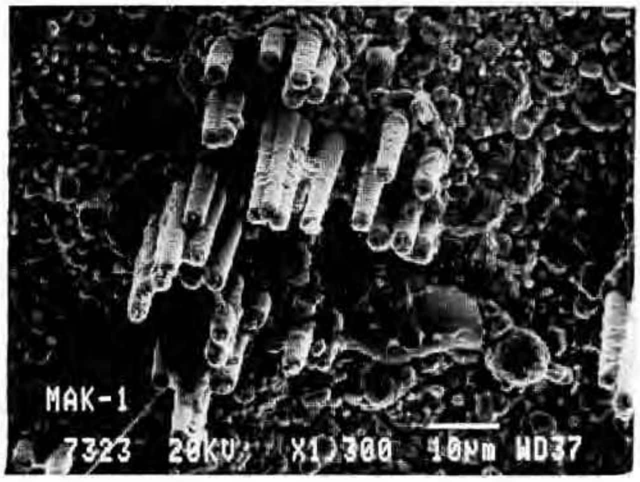

Fig. 3 — Microstructure ensembles of copper pins (coarse) produced by using ITFs of Makrofol-KG

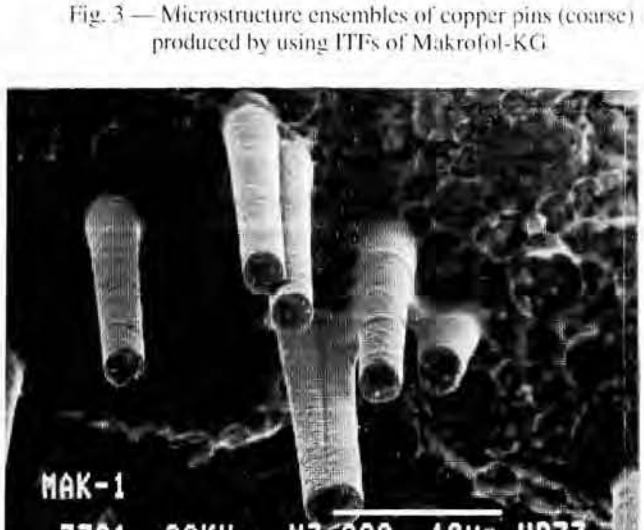

Fig. 4 — Microstructure ensembles of copper pins (fine) produced by using ITFs of Makrofol-KG

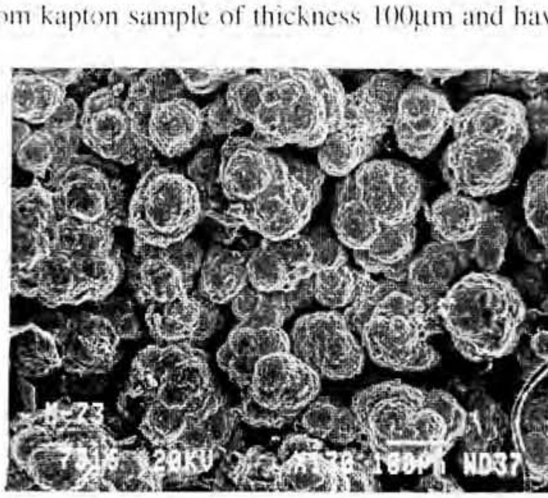

Fig. 2 — Top view of the grown copper buds due to prolonged deposition

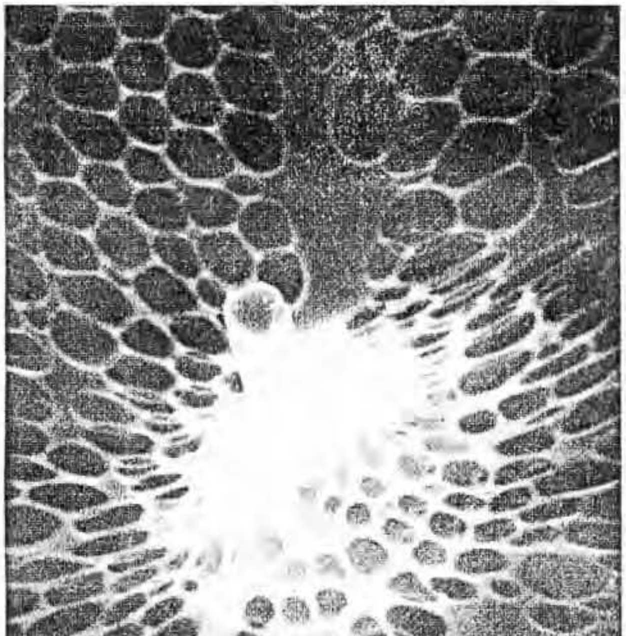

Fig. 5 — An isolated copper pin produced from ITF of Makrofol-KG

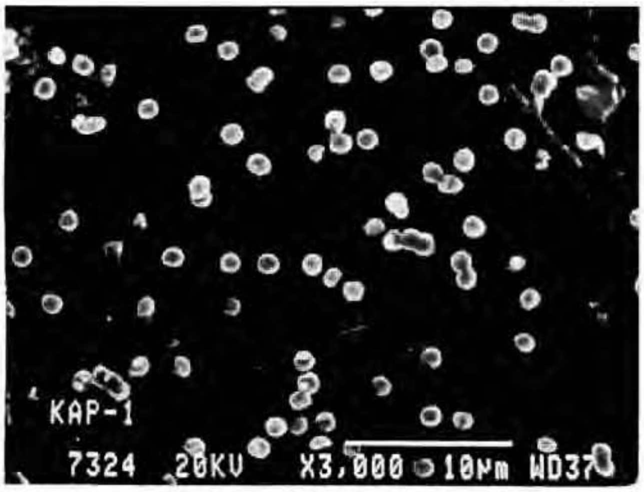

Fig. 6 — Projected top view of the copper pins developed by using ITFs of kapton

cal methods and replicas of etched tracks in ITFs used as template has two fold purpose. It provides the finest and critical details of the geometry and dimensions of microstructural constituent element and therefore enables to study the various aspects of interaction of a nuclear particle with the given material leading to for-

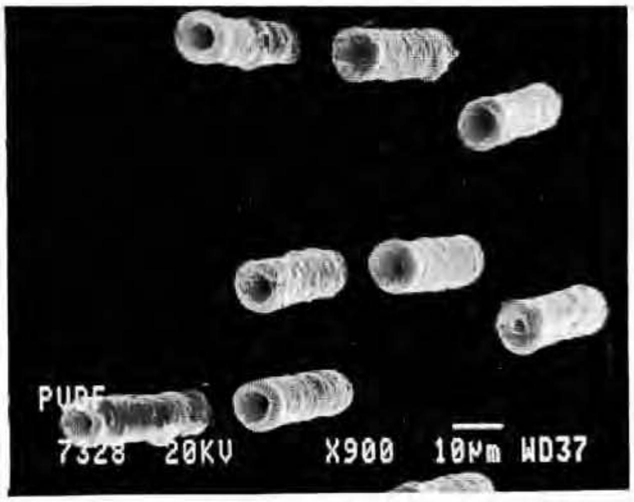

Fig. 7 — Microtubules developed by using the ITFs of PVDF

mation of tracks in ITFs. It is well known that parameters which control the shapes of tracks in ITFs include the nature of the material, the ion beam and its energy deposition rate (dE/dx), pre and post- irradiation storage, environment and the etch conditions. The metallic structures reveal the finer details of the constituents of the etched pores of ITFs. The etched ITFs containing micropores of suitable dimensions so as to reveal the morphological details, viz., diameter, length, shape (cylindrical, conical etc.) were used for track profile studies. The work is in progress to characterize the fabricated microstructures for device applications.

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