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Galvanic synthesis of copper microstructures on large areas of polymeric ion track membranes

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Abstract : 60 μm thick polycarbonate foils were irradiated to ^{208}Pb ions (energy~11.6 MeV/n, flux~10^7 ions/cm^2). Irradiated polycarbonate foils were chemically etched in 6N NaOH solution at 50(C for 25 minutes. Aligned copper microstructure bunches have been prepared by electrodeposition in porous polycarbonate templates from acidic copper sulphate solution at 25°C and 45°C respectively. Copper microstructures with uniform diameter ~ 1.5μm and length ~ 60μm were obtained, which corresponds to the pore sizes of the templates used. The XRD analysis of the samples has revealed that the copper microstructures are polycrystalline in nature

Keywords Microstructure; electrodeposition; template synthesis; ion track membranes

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1. Introduction

At present, nanowires have been the focal point of significant consideration because they have the prospective to answer elementary questions about one dimensional systems and are expected to play a central role in applications ranging from molecular electronics to novel scanning microscopic probes [1,2]. Investigation of such miscellaneous and stimulating prospects, requires nanowires materials for which the chemical composition and diameter can be of wide range [3, 4]. Over the past several years, substantial attempt has been made on the bulk production of nanowires and advances has been made using template, laser ablation, solution and other methods [5].

Electroplating is the most admired method now used for metal filling of pores in plastics and other insulating materials. The first man was the Possin [6], who deposited tin, indium and zinc into the etched tracks in natural mica by this method. Then Fischer and Spohr [7] patented a scheme for production of field emission cathodes based on the similar technique. Williams and Giordano [8] refined Possin's technique and reported growth of 8 nm thin gold wires. Penner and Martin [9] used electroplating for the preparation of ultramicro-electrodes using 10 mm thin polycarbonate membranes. Chakarvarti and Vetter [10-12] have applied electrodeposition of copper for the filling of pores in different organic foils irradiated with heavy ions and etched correspondingly to reveal some structural elements of ion track membranes. For better contact between the organic membrane and the cathode, they used convex shaped cathode surface. Prolonged metal deposition led to the formation of caps on the anode faced tops of metal needles, eventually merging to a closed metal layer.

This paper deals with the potential of Ion Track Membranes (ITMs) where conventional membranes lack completely. Secondary structures were obtained with the use of etched Ion Track Membrane technique [13]. A distinctive feature of the nano/microstructures obtained using this technique is the high uniformity of shape, size, orientation and their high surface density. The surface distributions of nano/microstructures are stochastic, which is the physical nature of the process of irradiation of the initial material with the high-energy ion beam.

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Such structures may find novel applications in microelectronics, micromechanics, optics and other fields [13-17].

2. Technique

With the emergence of very simple but potential particle track etch replication methods, a technique known as Template Synthesis has been developed, having the underlying principle akin to that of producing components through the use of replication *e.g.*, die casting or mold casting (like making ice candies out of molds), approaching through the etched pores as well as the walls of template membranes by either electrochemical or chemical reduction of appropriate metal ion. The generated structures can both be homogeneous or heterogeneous (including multilayers, short, squat fibrils, long needles, tubules, tapered conical *etc.*) depending on the pore size and geometry, with complete control over the aspect ratio (length to diameter ratio). Metallic and non-metallic tubules can be obtained by chemically derivation of the pore walls *i.e.*, by providing molecular anchors so that the electrodeposited metal preferentially deposit on the pore walls [11]. The template synthesis of metals usually carried out through galvanic replication technique by permitting the synthesis process on a metallic cathode substrate which is tightly covered by an etched Ion Track Membrane as an overlay and having the custom made pores which act as templates for growth of structures [13, 14]. In general, a suitable cell design is required and the layout design of such a cell along with other relevant details of the technique has been used [10,13].

3. Experimental

The schematic procedure for forming copper microstructures consists of several steps, as illustrated in Figure 1. Polycarbonate foils (Makrofol N, Bayer Leverkusen) of circular shape (thickness 10-60μm, diameter 5cm) were irradiated at the UNILAC (Universal Linear Accelerator) of GSI, Darmstadt, Germany with highly charged ^{208}Pb ions having kinetic energy of 11.6 MeV/n and fluences between 10^6 and 10^9 ions/cm^2. Due to energy loss through interaction with the target electrons, each ion creates along its trajectory a cylindrical damage zone of few nanometers in diameter. The damaged material can selectively be removed by chemical etching, resulting in pores of cylindrical geometry. Composition, concentration, and temperature of the etching solution decide the size and geometry of the resulting pores, the pore diameter increasing linearly with the etching time. In the present work, 60 μm thick polycarbonate foil irradiated to ^{208}Pb ions (11.6 MeV/n) having fluence of the order of 10^7 ions/cm^2, was used. 6N NaOH solution containing 10% methanol at T~50°C was employed for 25 minutes to produce pore diameter ~ 1.5μm. A thin layer of some noble metal (gold) was sputtered on one side of the membrane and then Copper tape (thickness 60 mm) having its base coated with conducting adhesive was fixed on sputtered thin gold layer to obtain a stable substrate, appropriate platform for the development of the needles. This conductive side served as cathode in a two-electrode electrochemical cell.

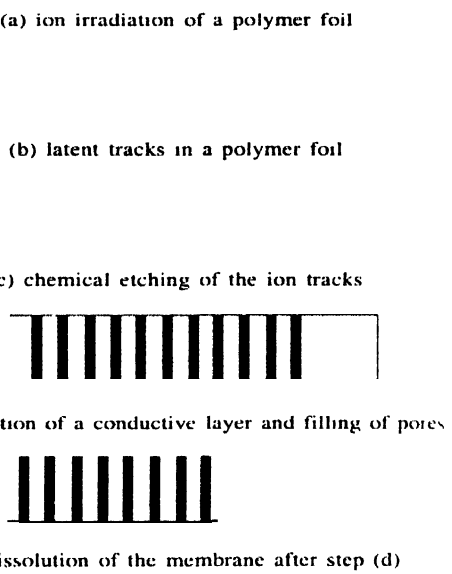

Figure 1. Scheme of the template synthesis method.

Simple-salt electrolyte that consisted of an aqueous solution containing 250 g/L $CuSO_4.5H_2O$ and 25 g/L sulfuric acid was used for copper electrodeposition. To supply a suitably huge number of ions inside the pores throughout the deposition process, high concentration of $CuSO_4.5H_2O$ was used. Sulfuric acid was added to enhance the conductivity of the solution. The electrodeposition was carried out potentiostatically at temperatures 25°C and 45°C respectively, with low over-voltages applied. The low over-voltages restrict side reactions such as hydrogen evolution.

Current was recorded as a function of time through out the electro-deposition process [Figure 2]. The measurements were performed in membranes irradiated under the same conditions and etched simultaneously (fluence 10^7 ions/cm^2, pore diameter 1.5μm). Four diverse zones (A-D) were obtained as indicated in Figure 2. When a potential is applied, the current exhibits a sharp decrease (A) that is attributed to the charge of the electrical double layer. In this process, the decrease of current depicts the creation of the diffusion layer [2,4]. During the development of the copper needles in the pores, the current remains nearly stable (B) until the wires arrive at the polymer surface. When this occurs, caps start to cultivate on top of the needles, and owing

to the increased surface, the current increases (C). Once caps are growing on the surface, the current keeps on rising very gradually (D).

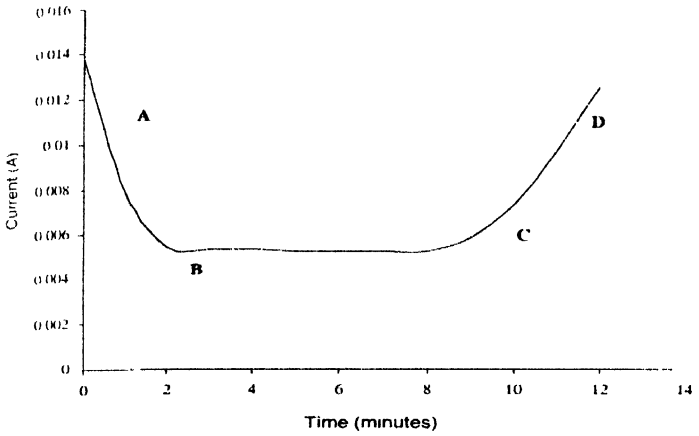

Figure 2. Variation of current with time during electrodeposition through pores in polycarbonate (diameter 1.5μm).

Afterwards, the membrane was dissolved in dichloromethane in order to image and characterize the copper microwires by scanning electron microscopy (SEM). The cleaned and dried samples were mounted on specially designed aluminium stubs with the help of double adhesive tape, coated with a layer of gold palladium alloy in JEOL, Fine Sputter Coater JFC 1100 sputter, coater and viewed under JEOL, JSM 6100 Scanning Electron Microscope at an accelerating voltage of 20KV. Images were recorded on the photographic film in the form of negatives at different magnifications. The SEM image of the Cu microstructures electrodeposited at 25°C and 45°C in the porous polycarbonate templates with pore size of about 1.5μm are shown in Figure 3(a) and Figure 3(b) respectively. Prolonged metal deposition led to the formation of caps on the anode faced tops of metal needles, eventually merging to a closed metal layer as clearly depicted in Figure 3(a). Figure 3(b) clearly depicts that electrodeposition at higher temperature reveals the best and clear microstructures.

Figure 3(a). SEM micrograph of Cu microstructures electrodeposited at 25°C having diameter 1.5μm.

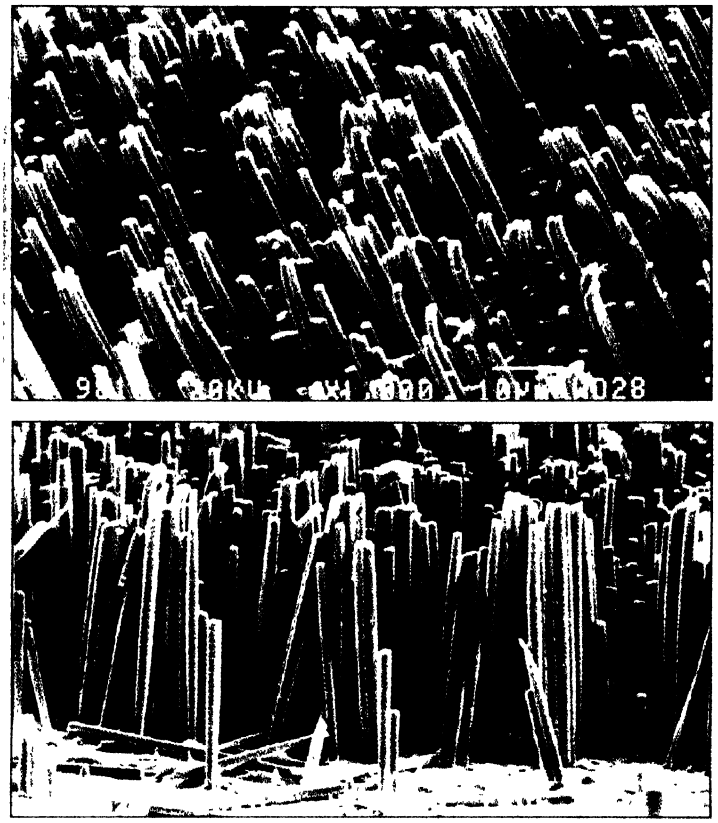

Figure 3(b). SEM micrograph of Cu microstructures electrodeposited at 45°C having diameter 1.5μm

X-ray diffraction measurements were carried out a Philips PW 1710 Diffractometer with Cu-K_α in θ/2θ mode. The XRD

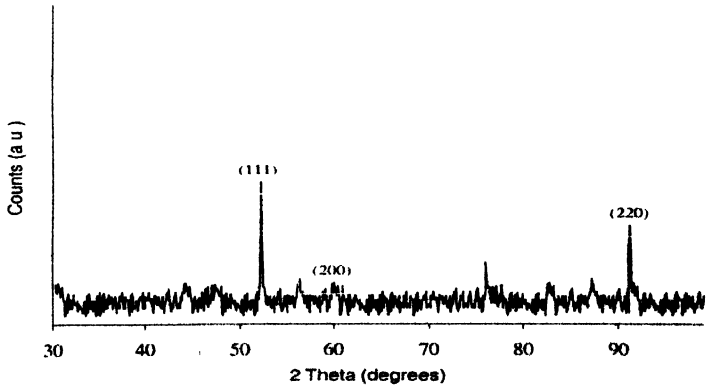

Figure 4(a). XRD diffractogram for Cu microstructures electrodeposited at 25°C.

analysis of the samples has revealed that the Cu microstructures deposited at 25°C are polycrystalline in nature [Figure 4(a)]. The wires deposited at 45°C showed a strong (200), (220) favored point of reference [Figure 4(b)], in spite of of the copper concentration and pH of the electrolyte used in deposition process. It has been observed that pH of the electrolyte has no consequence on the preferred orientation of the Cu microstructures though bath temperature had significant consequence on the crystallographic orientation of microwires [1,4]. XRD diffractograms clearly depicts that crystallinity improves with increase in electrodeposition bath temperature.

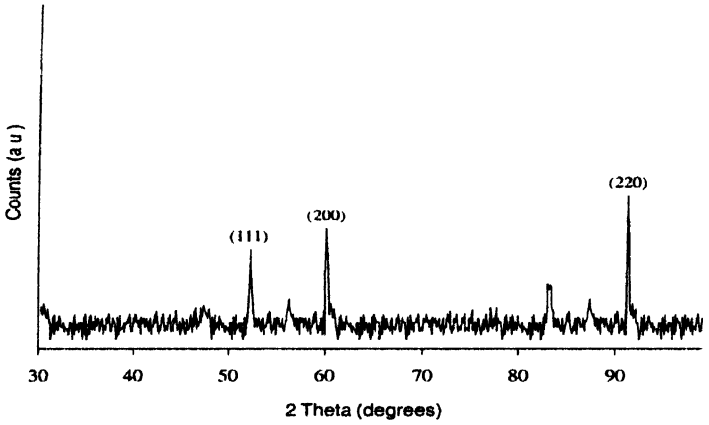

Figure 4(b). XRD diffractogram for Cu microstructures electrodeposited at 45°C.

4. Results and discussion

The production of needles with a large aspect ratio and micro and nanometers dimensions covering a huge surface area can be recognized by electrodeposition of metals in ion track membranes or anodized alumina membranes if: (a) good contact is accomplished between the host membrane and the cathode surface. (b) Suitable plating solutions as well as deposition circumstances are used, and (c) Standardized current supply over plated cathode surface is offered [14].

A good contact cannot be realized on a large area by pressing the matrix foil either to the flat or to the convex cathode surface. Coverage of the foil by sputtering or by evaporation is also insufficient. Therefore, in the technique used here one side of the matrix foil is made conducting by sputtering of a very thin metal layer [1-4] and then a copper tape (thickness 60 mm) having its base coated with conducting adhesive was fixed on sputtered thin gold layer to obtain a stable substrate. The foil is mounted in the two-electrode electrochemical cell so that the surface containing the thin conducting layer and fixed copper tape faces the anode. It blocks the pores from one side and serves in the next step as an adequate cathode [14].

A stable platform for the fabricated metal needles after removing the host membrane by dissolution or peeling was provided by the thick metal layer (thin gold layer + copper tape having conductive adhesive) on one side of the membrane. Supporting layer should be from the same metal as that used for pore filling. The choice of the electroplating baths and the associated deposition state of affairs are of key significance. A lot of baths for electroplating and electroforming have been devised for different metals. A large number of them have various organic and inorganic substances that improve the throwing power, brightness, ductility, hardness and other properties of the galvanic deposits [14]. The operating constraints of these baths are intended for normal plating conditions. Electrofilling of the pores considered here is rather different from normal electroplating, particularly at high aspect ratios of etched ion tracks.

There may be two mechanisms taking place simultaneously during electrochemical growth of the copper needles, [a] enlargement of existing nuclei and [b] nucleation followed by creation of fresh grains. For the formation of single crystals the first route should govern. The two routes contend with each other and depend on a number of constraints. In the present work reported in this paper, the influence of temperature on the resulting crystallinity of the needles has been considered. The increased temperature perceptibly leads to reduce the cathode polarization, to a more competent transfer of the ions towards the electrode, and to an enhancement of the surface diffusion [4]. We suppose that the additives are accountable for the large discrepancy of both the escalation rate and the crystallinity of the wires. When the simple-salt electrolyte is used, the copper deposition occurs at an apprenimately constant rate in all the pores over the entire sample and all wires demonstrate the identical crystallinity.

5. Conclusions

Template Synthesis is an elegant technique to prepare metallic nano/microstructures. We have successfully used this technique for the fabrication of copper microstructures having high aspect ratio. XRD diffractogram depicts the polycrystalline nature of Cu microstructures. The ITMs were etched so as to create micropores of appropriate dimensions so as to reveal the morphological details *viz.* diameter, length, shape (conical, cylindrical *etc.*) which are of interest for track profiling studies. This also assists the easy deposition of metals. With increase in electrodeposition bath temperature, crystallinity of copper microstructures improves. These microstructures can be used as field ion emitters, interconnects in microelectronics, sensors *etc.*

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