Electrochemical synthesis of metallic microstructures using etched ion tracks in nuclear track filters

Sanjeev Kumar[1,*], Rajesh Kumar[2], Shyam Kumar[1] and S. K. Chakarvarti[2]

[1]Department of Physics, Kurukshetra University, Kurukshetra 136 119, India
[2]Department of Applied Physics, National Institute of Technology (Deemed University), Kurukshetra 136 119, India

Interest in nano/microstructures results from their numerous potential applications in various areas such as materials and biomedical sciences, electronics, optics, magnetism, energy storage and electrochemistry. Materials with micro/nanoscopic dimensions not only have potential technological applications in areas such as device technology and drug delivery, but also are of fundamental interest in that the properties of a material can change in this regime of transition between the bulk and molecular scales. Electrodeposition is a versatile technique combining low processing cost with ambient conditions that can be used to prepare metallic, polymeric and semiconducting microstructures. In the present work ion track membranes of Makrofol (KG) have been used as templates for synthesis of metallic microstructures using the technique of electrodeposition.

MICROSTRUCTURE fabrication is not only of immense importance for microelectronics technology but also plays a vital role as a potent tool for carrying out investigations relating to behaviour of materials at sub-micron scales[1,2]. A variety of possible applications based on microstructures include high-power microwave generation, ultra-fast computer and tetra-hertz amplifier devices, radiation and temperature-insensitive electronics. Fields where well-established applications already exist include field emitters, electrochemistry, conductive polymer nanofibres fabrication, transparent metal structures and macroscopic quantum tunnelling phenomenon[3–18]. Of the many possible geometrical shapes and growth patterns, the simplest structure is probably an ensemble of wires. A variety of techniques like optical, X-ray, electron and ion beam lithography have been used for fabrication of such ensembles. However, electrochemical methods involving electrodeposition of metals into the etched pores of nuclear track filters (NTFs) of mica and polymers are a convenient and simple technique[3–13].

The morphological study of such structures produced through electrochemical methods and of replicas of etched tracks in NTFs used as templates, has a two-fold purpose. One, it provides the finest and critical details of the geometry and dimensions of microstructural constituent elements and the second, as a by-product it enables the study of various aspects of interaction of a nuclear particle with the given material leading to formation of tracks in NTF. It is well known that parameters which control the shapes of tracks in NTFs include the nature of the material, the ion beam and energy deposition rate, pre-and post-irradiation storage, and environment and the etching conditions. In the present work NTFs of Makrofol (KG) polycarbonate having pore size ca. 1 μm and pore density 1×10^6 cm^{-2} have been used as templates for synthesis of copper and nickel microstructures using the technique of electrodeposition (template synthesis). Because the membranes used contain cylindrical pores of uniform diameter, crops of monodisperse microstructures of the desired material, whose dimensions can be carefully controlled, are obtained.

Track etch membranes in the form of NTFs have emerged as a spin-off from solid state nuclear track detectors – solid dielectric materials capable of storing tracks of energetic, heavily ionizing ions. These tracks can subsequently be chemically amplified for optical observations as pores or channels of well-defined geometry and pore density[3–10]. The size and dimensions of the pores depend upon various factors, viz. the nature and energy of the incident ions, the target material, etch conditions, e.g. temperature and nature of the etchant. The pore size which is controllable, may range from a few nm to mm. NTFs have been put to numerous applications besides their use in the synthesis of nano/microstructures.

The underlying principle of template synthesis technique is akin to that of producing components through the use of replication, e.g. die-casting or mould-casting, like making ice candies out of moulds. In this technique, materials can be deposited within the template membranes by either electrochemical or chemical (electroless) reduction of the appropriate metal ion. The generated structures can be homogeneous or heterogeneous depending on the pore size and geometries, with complete control over the aspect ratio (length and diameter ratio). The simple and well known underlying concept of electrodeposition of metals through electroplating is described as an electrochemical process in which metallic ions in a supporting solution are reduced to the metallic state at the cathode, which if closely covered by an NTF membrane, would lead to the formation of growth of plated film as the embodiment of micro-or nanostructure. The etched pores of the membranes would act as templates[3–15].

Production of stable metal structures by electrodeposition using etched ion tracks in various insulator materials as templates includes the following steps as illustrated in Figure 1: (a) Ion irradiation of a polymer foil; (b) Generation of latent tracks in polymer foil; (c) Chemical etching of the ion tracks and sputtering of a conductive film onto one side of the membrane; (d) Electrodeposition of the pores through their open side; (e) Removing of the host template by dissolution of the membrane.

*For correspondence. (e-mail: bhogrask@yahoo.co.in)

The method described was checked by deposition of copper and nickel in pores of polycarbonate membranes. Samples of polycarbonate of thickness 15 μm were irradiated with 13.64 MeV/n ^{238}U ions (fluence 10^6 ions/cm^2) utilizing the heavy ion accelerator UNILAC facility at GSI, Darmstadt, Germany. Samples were etched in 6N NaOH solution at 60°C for 20 min and pore size of 1 μm was obtained. After etching, this NTF having pore size 1μm and pore density $10^6/cm^2$ is used for synthesis of metallic microstructures using the technique of electrodeposition. Because the membranes used contain cylindrical pores of uniform diameter, crops of monodisperse microstructures of the desired material, whose dimensions can be carefully controlled, are obtained. The electrodeposition of metal would take place through pores whose dimensions and geometry, therefore, would dictate the morphology and geometry of the nascent microstructure produced.

The electrolyte used was $CuSO_4.5H_2O$ (200 g/l) + H_2SO_4 (20 g/l) in Milli Q 18 MΩ water for copper deposition. The pH of the solution used was adjusted to be 0.90. The electrodeposition was carried out for 12 min at 0.8 V (current 0.0137–0.0140 A) at room temperature (nearly 25 ± 2°C) with a pure copper sheet as anode. After completion of electrodeposition, the electrolyte was drained out and the cathode flushed with 3% H_2SO_4, followed by Milli Q water rinsing and air-drying. For Makrofol NTFs, CH_2Cl_2 was used as solvent followed by rinsing with water and ethanol[3–6].

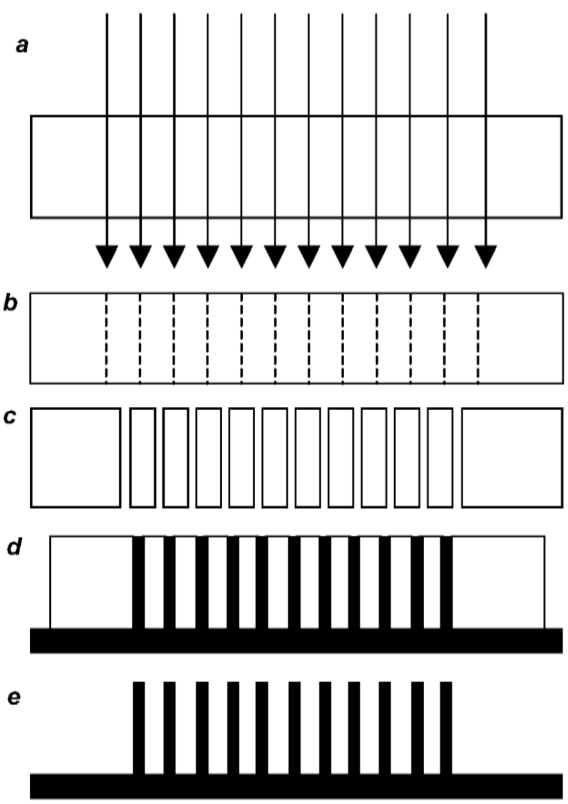

Figure 1. Schematic diagram of the template technique used. ***a***, Ion irradiation of a polymer foil; ***b***, Latent tracks in a polymer foil; ***c***, Chemical etching of ion tracks; ***d***, Deposition of a conductive layer and filling of pores; ***e***, Dissolution of membrane after step (***d***).

During the deposition process, we recorded the electrical current as a function of time. A typical chronoamperometric curve is presented in Figure 2. In general, four different zones can be distinguished. The sharp current decrease at the beginning of the process (I) is ascribed to the charge of the double layer and the creation of the diffusion layer. During the growth of the needles in the pores, the current remains nearly constant (II). As soon as the wires reach the upper surface, caps are formed and the current increases (III). Finally caps are growing to macroscopic sizes at an almost constant rate (IV). The deposition process was stopped either during phase II (to characterize the needles) or in phase IV (to observe the caps).

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 JFC 1100 sputter and viewed under JEOL, JSM 6100 Scanning Microscope at an accelerating voltage of 20 kV. Images were recorded on the photographic film in the form of negatives at different magnifications. The metallic microstructures with stochastically distributed elements reveal finer details of the constituents and of the etched pores of the host NTF. Figure 3 shows the SEM micrographs of copper microstructures. Similarly, for nickel deposition, the electrolyte used consisted of 60 g/l $NiSO_4$ and 30 g/l H_3BO_3. Deionized water with resistivity ~ 18 MΩ was used to prepare the solution. Deposition was carried out at a slightly higher temperature (at 40 ± 2°C). Figure 4 shows the SEM micrographs of nickel microstructures.

As the shape of the wires directly reflects the geometry of the pores in the polycarbonate, there is clear evidence

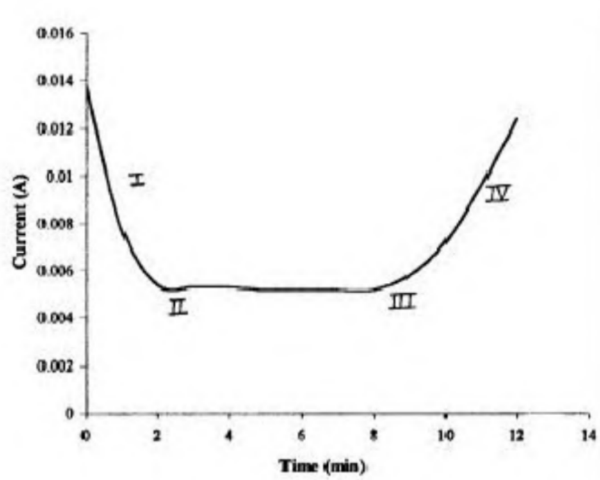

Figure 2. Variation of current with time during electrodeposition of copper.

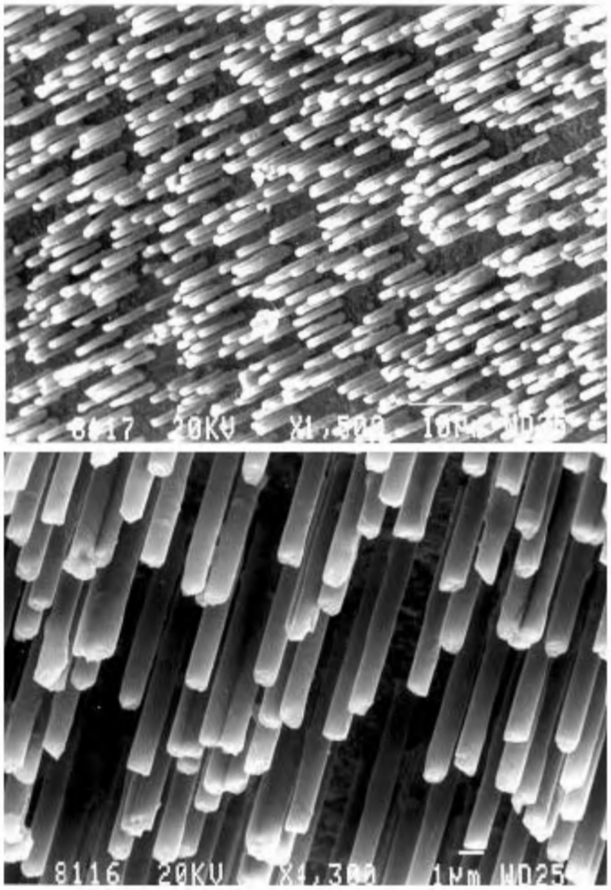

Figure 3. Scanning electron micrographs of large-scale array of copper microstructures.

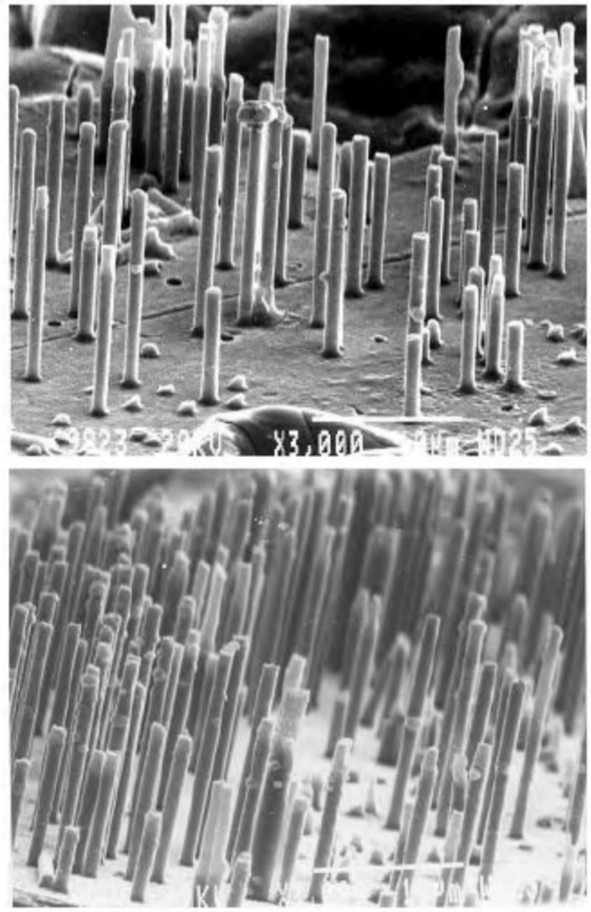

Figure 4. Scanning electron micrographs of nickel microstructures.

that under the employed irradiation and etching conditions, the pores are well aligned and have cylindrical geometry. It should be emphasized that needles with cigar shapes as discussed by several authors[12], were never observed. We assume that such an effect is linked either to special properties of the polymer or caused by additives to the etchant solution (e.g. surfactants)[13]. The surface smoothness of the wires depends on several factors such as the quality of the polymer and etching process. Our observations strongly indicate that the conditions during deposition also play an important role. The presence of air bubbles in the pores, hydrogen evolution during depositions at very high over-voltages, or bad quality of the deposited metal at very high current densities result in rather large roughness of the wire surface. The property of our templates can be of great importance if homogeneous needle growth is required. Problems due to large angular distributions, with tilt angles of more than 30°, in commercially available membranes have been reported[14]. Polycarbonate membranes, as presented here, provide suitable templates for basic research and for applications where a high degree of parallelism is of importance.

In conclusion, the template method is a simple yet powerful process for the synthesis of nanomaterials. We have demonstrated that metallic microstructures can be prepared using electrochemical deposition. Copper and nickel microstructures were synthesized without prior treatment of the membrane pores with a molecular anchor. This study opens a new path for fabricating magnetic microstructures, which may serve as new interconnects in micrometre-scale electronic devices. Applications have ranged from fundamental optical studies to ultra trace molecular detection to high surface-area catalysis.

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Electronic biopsy for skin cancer detection

G. Florence Sudha* and T. Ganesa Palnivelu

Department of Electronics and Communication Engineering, Pondicherry Engineering College, Pondicherry 605 014, India

Assessing tissues without their removal is a great advantage. A tissue biopsy removes tissue, which yields a wound that requires healing. Healing may cause discomfort to the patient and may yield a scar. This communication proposes an optoelectronic biopsy, employing light source and optical fibres. This reflectance imaging system permits imaging of the tissue so as to discriminate the cancerous ones without removal of tissues for analysis. This system based on the principle of backscattering of laser radiation from tissue promises to be a low cost, accurate and fast tool for detection of skin cancer.

SKIN cancer is the most frequently occurring of all cancers. Each year over 500,000 new cases of skin cancer are detected. In a high percentage of skin cancers fatalities can be all but eliminated and morbidity reduced, if detected early and treated properly. These skin lesions are distinguished generally by subjective visual inspection and their definitive diagnosis requires time-consuming, expensive histopathological evaluation of excisional or incisional biopsies.

There are three main types of skin cancer–malignant melanoma, basal cell carcinoma and squamous cell carcinoma. Melanoma is less common, but the most serious type. It can spread if not detected at an early stage. It often spreads to other tissues or vital organs. Melanomas are irregular in shape, show variation in colour and are lesions bigger than 6 mm across. Basal cell carcinoma is the most common type of skin cancer. It grows slowly and can damage nearby tissues. It arises from cells in the epidermis. It is not life-threatening, but if left untreated, cancerous cells can grow deeper into the skin. Squamous cell carcinoma is the most common type of skin cancer. It arises from cells in the epidermis and can spread to nearby lymph nodes. It can be dangerous because it grows more quickly.

Other skin infections are Actinic keratosis and Bowen's disease that can become malignant. The condition is harmless, but if left untreated it may transform to squamous cell carcinoma. Seborrheic keratosis is a benign form of skin tumour occurring in the outer layers of the skin. Compound nevus is characterized by proliferation of nevus cells within the basal cell layer of the surface epithelium and the underlying connective tissue.

Currently, the majority of skin cancers are confirmed using an invasive biopsy. This means that a section of the

*For correspondence. (e-mail: gfsudha@eth.net)