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ELECTRODEPOSITION OF COPPER NANOWIRES IN ION-CRAFTED MEMBRANES AS TEMPLATES

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Copper nanowires have been synthesized using potentiostatic electrodeposition within the confined nanochannels of a porous ion-crafted membrane. Morphology of electrodeposited copper nanowires has been studied using scanning electron microscopy. These nanowires have uniform diameters of about 100 nm, which corresponds to the pore size of the templates used.

Keywords: Copper electrodeposition, Nanowires, Templates and membranes

1. Introduction

In the current era of technology there is continuously nonstop advancement in miniaturization of electronics components. But, the laws of quantum mechanics, the restrictions of production method and the rising expenditure of the production facilities may rapidly avert us from the more scaling down of conventional silicon technology. The hunt for substitute technologies has motivated a surge of curiosity in nanometer-scale materials and devices in current years. For the reason that of their exceptional characteristic metal nanowires are one of the majorities striking materials that may escort to a variety of applications [1-6]. Examples comprise interconnects for nanoelectronics, magnetic devices, chemical and biological sensors, etc [7-10].

To generate regular periodic arrays of submicron wires, dots and pillars advanced lithographic procedures are presently engaged. As an alternative, to produce arrays of metal nanowires, electrochemical deposition of metals into porous templates is executable. For the most part frequently used templates are ion-crafted membranes. This technique is known as template synthesis. Excellent reviews are available regarding this technique [10-14]. This technique has the striking features of extreme simplicity in operation and high cost-effectiveness.

Ion-crafted membranes also known as ion track membranes (ITMs)**,** besides their utility in microelectronics, find immense applications in areas such as materials science. In materials science, ITMs act as templates [1-16] for the deposition of desired materials leading to the development of nano/micro-structures. Such structures may be used as field emitters [15], micro diode arrays [5], conducting polymeric fibrils [8], super-conducting wires [16], magnetic data storage devices [17], transparent metal microstructures [9] etc. Ion track membranes filled with photosensitive materials may also act as flexible solar cell panels [11]. In bio-medical applications, ion track membranes can be used to synthesize polymeric microcapsule arrays for enzyme immobilization for use in biosensors and bioreactors [8] besides their use as filters. Such membranes also play important role in drug delivery devices. In chemical sciences, template synthesized nano/microstructures can be used as pH sensors and as an accurate measuring device for minute solute concentration in solutions [11].

Further, as discussed above, the ion track membrane based template synthesis leads to the generation of nanomaterials. In recent days, such materials have gained importance because of the fact that when the material size approaches nanoscopic dimensions, the properties of a material can altogether change [10-14]. As a result, there is now an extensive curiosity being exhibited in the elemental understanding of nanomaterial properties and in their potential use for technological applications in diverse areas. In the present work, copper nanowires were electrochemically synthesized using etched pores in polycarbonate ion track membrane. Morphology of electrodeposited copper nanowires has been studied using scanning electron microscopy. These nanowires have uniform diameters of about 100 nm, which corresponds to the pore size of the templates used.

2. Materials and methods

Ion track membranes (ITMs), also known as Nuclear Track Filters (NTFs), have emerged as spin-off from Solid State Nuclear Track Detectors (SSNTDs) - solid dielectric materials proficient of storing latent tracks of energetic heavy ions, which can consequently be chemically enlarged for optical inspection as pores or channels of well defined geometry and density. The size or dimensions of the pores depend upon different factors viz. the nature and energy of the incident ions, the target material, etching conditions etc. [10-14]. Incident ions with suitably high energies competent of crossing the detector sheet entirely leads to the creation of through tracks, which become see-through channels in the detector sheets. These act as ion track membranes (ITMs) or nuclear track filters (NTFs). Under controlled etching conditions, these see-through channels can be enlarged to preferred size and shape.

The fundamental principle of template synthesis method is similar to that of producing components through the use of replication e.g. die-casting or mold casting, like making ice candies out of molds. In this technique, materials can be deposited with in the template membranes by either electrochemical or chemical (electroless) reduction of the appropriate metal ion. Many good and informative articles have described a host of chemistries that are now available for the template synthesis of a wide variety of nanomaterials including metals, polymers and semiconductors [10-14]. The generated structures can both 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 basic 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 is closely covered by an ITM, would lead to formation of escalation of plated film as the incarnation of micro or nano structure.

3. Experimental

15 μm thick polycarbonate foils (Makrofol N, Bayer Leverkusen) were irradiated with heavy ions ^{58}Ni (sp. energy 11.4MeV per nucleon) at normal incidence using UNILAC facility at GSI, Darmstadt, Germany. Fluence of 10^7 ions/cm^2 was applied. The irradiated foils were chemically etched at 50 °C for 12 minutes in 6N NaOH solution containing 10% methanol. The resulting pores are cylindrical, their diameters increasing linearly with the time of etching. Fig. 1. presents the SEM micrograph of etched pores in ion-crafted polycarbonate membrane. A thin copper layer was sputtered onto one side of the polymer membrane. Sputtered metal layer on the one side of the membrane served as cathode in our two-electrode electrochemical cell. Pure copper rod was used as anode. The electrolyte consisted of an aqueous solution of 280 g/l $CuSO_4.5H_2O$ and 25 g/l H_2SO_4. High concentration of $CuSO_4$ is important to provide a sufficiently large number of copper ions inside the pores during the galvanic deposition process. Electrodeposition was performed potentiostatically at room temperature i.e 29±1°C. During the deposition process, we recorded the electrical current as a function of time. Fig. 2 shows the current versus time graph during electrodeposition process.

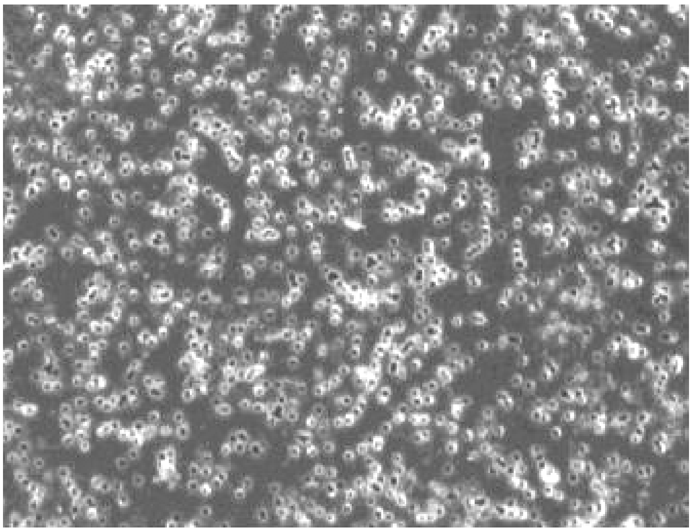

Fig. 1. SEM micrograph of etched pores in ion-crafted polycarbonate membrane.

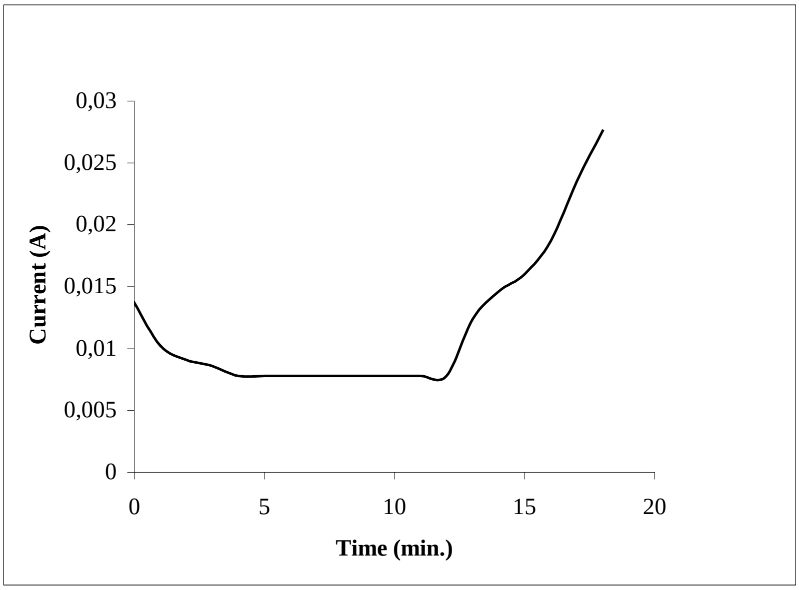

Fig. 2. Variation of electrical current as a function of time during electrochemical deposition process.

After the deposition the polycarbonate templates with Cu nanowires were immediately removed from the electrolyte, first rinse with double-distilled water and ethanol, finally dried in dry air at room temperature and subjected to further analysis. The porous polycarbonate membrane was removed by dissolving it in dichloromethane for 10 minutes and washing with several times with double-distilled water. 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, coater and viewed under “Jeol, JSM 6100 Scanning Microscope” at an accelerating voltage of 30 KV. Images were recorded on the photographic film in the form of negatives at various magnifications. Fig. 3. represent SEM micrographs of electrodeposited copper nanowires after the dissolution of host ion-crafted polycarbonate membrane.

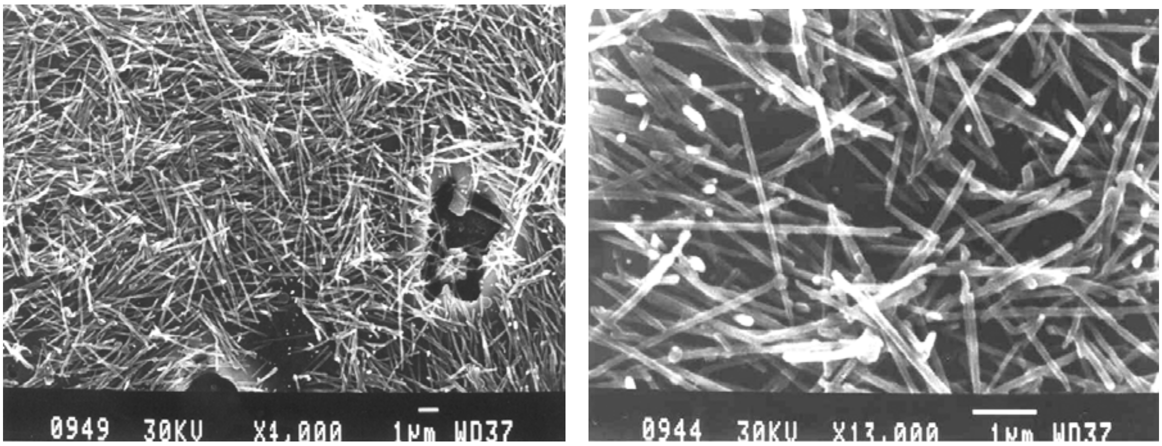

Fig. 3. SEM micrographs of electrodeposited copper nanowires after the dissolution of host ion-crafted polycarbonate membrane.

4. Discussion

The ITMs offer distinct advantages for their use as templates for the generation of nano/microstructures over other host membranes like alumina membranes, nanochannel array glass membranes, xeolites etc. This is because in ITMs, pore density, pore shape and aspect ratio can be controlled [1-6] as per the specific requirements by suitably choosing incident ion beam from the accelerator and the etching conditions.

Some unique properties of ITMs are (i) adjustable pore diameter ranging from 15 nm to 0.6 mm depending on the incident ion, target material parameters and etching conditions, (ii) single particle drilling tool, each pore corresponds to single particle hit, (iii) narrow pore size distribution mainly dependent on homogeneity of the recording material, (iv) uniform pore diameter and length depending on incident particle parameters and thickness of the recording material, (v) uniform orientation of pores (parallel to each other within ± 1°) and (vi) adjustable density of pores (10^0 to 10^{10} pores/cm^2).

The morphological study of such structures produced through electrochemical methods and of replicas of etched tracks in ITMs used as templates, has two-fold purpose. One, it provides the finest and critical details of the geometry and dimensions of micro structural constituent elements and the second, as a by product it enables to study the various aspects of interaction of a nuclear particle with given material leading to formation of tracks in ITM. It is well known that parameters, which control the shapes of tracks in ITMs, include the nature of the material; the ion beam and energy deposition rate; pre, post-irradiation storage and environment and the etching conditions [10-14].

5. Conclusions

The template method has become a very simple yet prevailing process for the creation of nanomaterials. Polycarbonate membranes, as reported in this paper, provide suitable templates for basic research and for applications where a high degree of parallelism is of vital significance [1-3]. During the copper deposition process, the Cu^{+2} ions deposit onto the cathode surfaces from the solutions to engender copper grains, and cultivate in the form of wires owing to the confinement consequence of the nanochannels [1-3].

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References

[1] E. M. Toimil Molares, J. Brotz, V. Buschmann, D. Dobrev, R. Neumann, R. Scholz, I. U. Schuchert, C. Trautmann, J. Vetter, Etched heavy ion tracks in polycarbonate as template for copper nanowires; Nucl. Instr. and Meth., B **85**, 192 (2001).
[2] E. M. Toimil Molares, E. M. Hohberger, C. Schaeflein, R. H. Blick, R. Neumann, C. Trautmann, Electrical characterization of electrochemically grown single copper nanowires; Appl. Phys. Lett. **82**, 2139 (2003).
[3] I. Enculescu, Z. Siwy, D. Dobrev, C. Trautmann, Toimil M. E. Molares, R. Neumann, K. Hjort, L. Westerberg, R. Spohr, Copper nanowires electrodeposited in etched single-ion track templates; Appl. Phys. A **77**, 751 (2003).
[4] M. E. Toimil Molares, N. Chtanko, T. W. Cornelius, D. Dobrev, I. Enculescu, R. H. Blick, R. Neumann, Fabrication and contacting of single Bi nanowires; Nanotechnology 15, No. 4 (April 2004) S 201.
[5] M. Sima, I. Enculescu, T. Visan, R. Spohr, C. Trautmann, Electrochemical deposition of PbSe1-xTex nanorode and nanotube arrays using track etch membranes as template; Molecular Crystals&Liquid Crystals 418, (2004) 21(749).
[6] M. Sima, I. Enculescu, C. Trautmann, R. Neumann, Electrodeposition of CdTe nanorods in ion track membranes; J. Optoelectron. Adv. Mater. **6**, 121 (2004).
[7] E. Ferain, R. Legras, Track-etch templates designed for micro- and nanofabrication, Nucl. Instr. and Meth., **B208**, 115 (2003).
[8] L. D. Pra, E. Ferain, R. Legras, S. D. Champagne, Fabrication of a new generation of track-etched templates and their use for the synthesis of metallic and organic nanostructures, Nucl. Instr. and Meth., B196, 81 (2002).
[9] A. Huczko, Template-based synthesis of nanomaterials; Appl. Phys. A **70**, 365 (2000).
[10] E. Ferain, R. Legras, Characteristics of nanoporous particle track etched membrane; Nucl. Instr. and Meth., **B131**, 97 (1997).
[11] C. R. Martin, Nanomaterials: a membrane based synthetic approach; Science, **266**, 1961 (1994).
[12] C. Schoenberger, B. M. I. vander Zande, L. G. F. Fokkink, M. Henny, C. Schmid, M. Kruger, A. Bachtold, R. Huber, H. Birk, U. Staufer, Template Synthesis of Nanowires in Porous Polycarbonate Membranes: Electrochemistry and Morphology; J. Phys. Chem. B. **13**, 5407 (1997).
[13] S. K. Chakarvarti, J. Vetter, Template synthesis-A membrane based technology for generation of nano/micro materials: A Review; Rad. Meas. 29 (2), 149 (1998).
[14] S. K.Chakarvarti, J. Vetter, Morphology of etched pores and microstructures fabricated from nuclear track filters; Nucl. Instr. and Meth., **B62**, 109 (1991),.
[15] Vila L., P. Vincent, L. D. Pra, G. Pirio, E. Minoux, L. Gangloff, S. D. Champagne, N. Sarazin, E. Ferain, R. Legras, L. Piraux, P. Legagneux (2004), Growth and field emission properties of vertically aligned cobalt nanowires arrays, Nano Letters, 4(3), 521-524.
[16] S. Michotte, L. Piraux, S. Dubois, F. Pailloux, G. Stenuit, J. Govaerts, Superconducting properties of lead nanowire arrays, Physics C, 377, (2002) 267.
[17] A. Fert, L. Piraux, Magnetic nanowires, J. Mag. Mag. Mater. **200**, 338 (1999).