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Effect of over-potential on the surface morphology of electrodeposited copper micro-cylinders

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60 μm thick polycarbonate foils were irradiated to ^{208}Pb ions (energy~11.6 MeV/n, flux~10^6 ions/cm^2). Irradiated polycarbonate foils were chemically etched in 6N NaOH solution at 60 °C for 35 minutes. Aligned copper microstructure bunches have been electrodeposited in porous polycarbonate templates from acidic copper sulphate solution at 30°C. Copper microstructures with uniform diameter ~ 3 μm and length ~ 50 μm were obtained, which corresponds to the pore sizes of the templates used. Effect of over-potential on the surface morphology of electrodeposited micro-cylinders was also observed.

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1. Introduction

The surface morphological survey of copper electrodeposits generated from acidic copper sulphate solutions was widely examined [1,2]. It was also reported that in the region of overpotentials corresponding to the activation control of deposition procedure, the grains with well-defined crystal planes are produced.

Currently nanowires have been the crucial point of noteworthy attention because they have the potential to answer basic queries about one dimensional structures and are likely to contribute a vital role in applications ranging from molecular electronics to novel scanning microscopic probes [3-5]. To scrutinize such assorted and exciting prospects needs nanowires materials for which the chemical composition and diameter can be convenient [6-7]. Over the past several years' extensive effort has been sited on the bulk fabrication of nanowires and while progress has been made using template, laser ablation, wet chemical solution, advanced lithography and other methods [5].

Electroplating is the majority-accepted technique used for metal filling of pores in plastics and other insulating materials. Possin [8] was the first who deposited tin, indium and zinc into the etched tracks in natural mica using this technique. Spohr [9] patented an idea for creation of field emission cathodes based on the analogous technique. Williams and Giordano [10] reported growth of 8 nm thin gold wires utilizing similar technique. Penner and Martin [11] fabricated ultramicro-electrodes using 10 μm thin polycarbonate membranes. Chakarvarti and Vetter [12-13] reported on synthesis of microstructures of metals, non-metals and semiconductors using track-etch membranes via template synthesis. Further the synthesis of nano/micro devices like resonant tunneling diodes have also been reported using track-etch membranes as templates [14]. A review of the template synthesis technique using membranes as templates is available in the literature [15].

A unique feature of the nano/microstructures obtained using this technique is the elevated 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. Such structures may find novel applications in microelectronics, micromechanics, optics and other fields [12-20].

In the present work Aligned copper microstructure bunches have been electrodeposited in porous polycarbonate templates from acidic copper sulphate solution at 30 °C. Effect of over-potential on the surface morphology of electrodeposited micro-cylinders was also studied.

2. Experimental

Polycarbonate foils (Makrofol N, Bayer Leverkusen) of circular shape (thickness 10-60 μm, diameter 5 cm) 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 10^6

ions/cm^2 was used. 6N NaOH solution containing 10% methanol at T~60 °C was employed for 35 minutes to produce pore diameter ~3 μm (Fig. 1). Copper tape (thickness 60 μm) having its base coated with conducting adhesive was fixed on one side of the membrane 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.

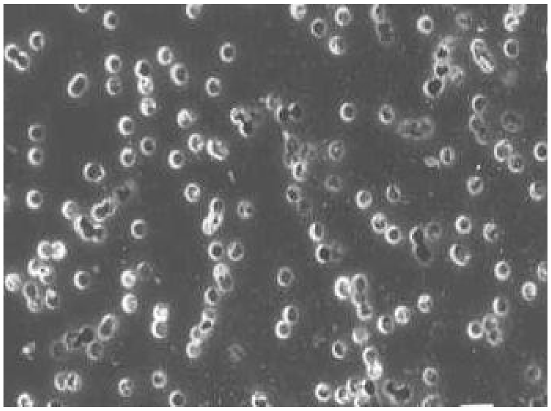

Fig. 1. SEM micrograph of etched pores in ion track membrane.

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. Doubly distilled water and analytical grade chemicals were used for the preparation of the solution for the electrodeposition of copper. 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. Two-electrode cell was used for the electrodeposition. Counter electrode used was of pure copper. The electrodeposition was carried out potentiostatically at temperature 30°C. 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 (Fig. 2).

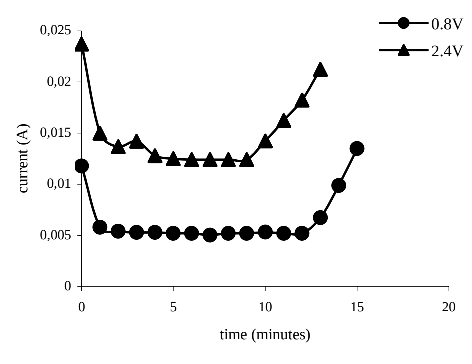

Fig. 2. Variation of current with time during electrodeposition through pores in polycarbonate.

Afterward, 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 20 KV. Images were recorded on the photographic film in the form of negatives at different magnifications. The SEM image of the Cu microstructures electrodeposited at 0.8V & 2.4 V in the porous polycarbonate templates with pore size of about 3μm are shown in Fig. 3 & Fig. 4 respectively.

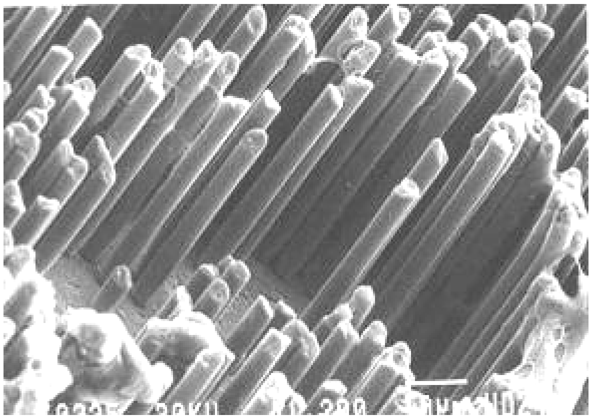

Fig. 3. SEM micrograph of Cu microstructures having smooth surfaces electrodeposited at 0.8V.

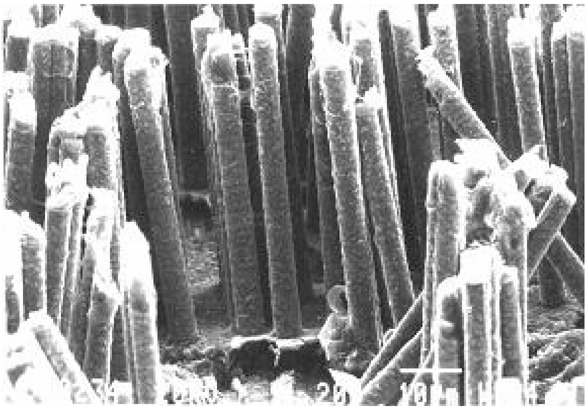

Fig. 4. SEM micrograph of Cu microstructures having rough surfaces electrodeposited at 2.4V.

3. Results and discussion

For studying the effect of over-potential on copper deposition PC ITM was divided into two equal parts having same size of etched pores. In the first part copper was electrochemically deposited at 0.8V at room temperature while in the second part copper was deposited at 2.4V at room temperature. The Fig. 3 shows the SEM micrograph of copper microstructures grown at 0.8V. Fig. 4 shows the SEM micrograph of copper microstructures grown at 2.4V. From these figures it is clearly evident that copper microstructures deposited at 0.8V are smoother than that those deposited at 2.4V. High over-potential induces the rapid deposition of copper ions in the pores and causes the production of structures having rough surfaces due to over-depositions.

The average current is approximately double at the overpotential 2.4V than at the lower potential 0.8V. The obtained morphologies of copper microstructures can be explained by the following consideration. It is known that the hydrogen evolution effects onto the hydrodynamic conditions inside electrochemical cell. The increase in hydrogen evolution rate leads to the reduction of diffusion layer width and hence to increase of limiting diffusion current density of electrode processes.

In the absence of hydrogen evolution, the diffusion layer is due to the natural convection and does not depend on the applied potential. The intensive hydrogen evolution changes the hydrodynamic conditions and decreases the degree if diffusion control.

The concept of effective overpotential was already reported [2] on the basis of the obtained morphologies of copper deposits. According to this concept, at lower applied potentials during electrodeposition there is no change in the shape morphology because contribution of hydrodynamic effects is negligible. But at higher overpotentials a tremendous change in surface morphology of electrodeposits was observed and this is due to the change in hydrodynamic conditions which was further caused by the intensive stirring of the copper solution in the near electrode layer by evolving hydrogen.

The fabrication of pillars with a great aspect ratio and having micro/nanometer dimensions covering a vast surface area can be predictable by electrodeposition of metals in anodized alumina membranes or ion track membranes if: (a) consistent current supply during electrodeposition over cathode surface is offered (b) appropriate electrolytic solutions as well as deposition circumstances are used, and (c) fine contact is accomplished between the cathode surface and the host membrane [5-6].

4. Conclusions

In conclusion 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. The applied potentials used in the potentiostatic ECD processes for the fabrication of copper microstructures have great influence on the surface morphology of the products. Copper microstructures having smooth and clean surface can be prepared by choosing suitable applied potentials in the potentiostatic ECD processes. Lower overpotentials are required for preparing copper microstructures having smooth and clean surface. At higher overpotentials hydrogen evolution affects greatly the surface morphology of electrodeposited copper microstructures.

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