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Fabrication of Copper Nanowires by Electrodeposition using Anodic Alumina and Polymer Templates

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Abstract

Copper is one of the most important metals in modern electronic technology. Keeping in view its role in nanoelectronics, we have fabricated copper nanowires of diameters 100 and 200nm using Anodic Alumina and polymer membranes as templates. Electrodeposition technique based on the principle of electroplating was adopted for copper nanowire fabrication in an electrochemical cell designed in our laboratory. SEM micrographs are used to calculate the aspect ratio of nanowires. The morphology of nanowires shows some interesting features.

Introduction

During recent years, nanowires and nanorods of metallic and semi-conducting materials have drawn a lot of research interest because of their potential applications in diverse fields, for example, nanoelectronics, opto-electronics and sensors. The special features of nanowires are defined by two quantum-confined dimensions allowing free flow of current in one dimension only. In nanowires, electronic conduction takes place both by bulk conduction and through tunneling mechanism. However, due to their high density of electronic state, diameter-dependant band gap, enhanced surface scattering of electrons and phonons, increased excitation energy, high surface to volume ratio and large aspect ratio, nanowires of metals and semiconductors exhibit unique electrical, magnetic, optical, thermoelectric and chemical properties compared to their bulk counterpart [1,2].

Many studies have focused on the fabrication of copper nanowires [3-6], because of their potential applications in the micro/nanoelectronics industry and, in particular, for interconnection in electronic circuits. Copper is one of the most important metals in modern electronic technology. Many methods have been developed for the fabrication of copper nanowires but template synthesis is considered to be most suitable and useful for growth of nanowires. Electrochemical deposition route is easy, low-cost as well as less cumbersome compared to other fabrication techniques, namely, pulsed laser deposition (PLD), vapour-liquid-solid (VLS) method and chemical vapour deposition (CVD) [1]. Electrochemical cell used in electrodeposition of copper into pores of anodic alumina template was fabricated in our laboratory. Morphology of electrodeposited copper nanowires has been studied using scanning electron microscopy (SEM). The diameter of nanowires depends upon the pore size of template. Anodic alumina discs of 200 nm pore diameter and polymer membranes of 100 nm pore diameter were selected for this purpose.

Materials and Methods

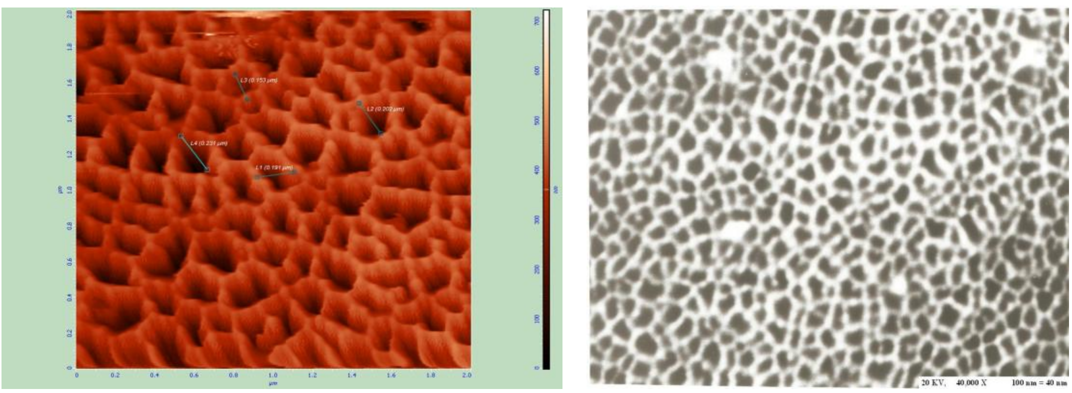
Electrodeposition technique used in our experiment is similar in principle to that used for the electroplating process. Commercial anodic alumina membranes (Anodisc 25, Whatman, U.K.) having an average pore diameter of 200 nm, a nominal thickness of 60 µm and pore density of 10^9 pores/ cm^2, were used as templates. A second set of polymer membranes was selected for sake of comparison. Commercially available polycarbonate membranes (Sterlitech, USA) of 25 mm diameter with pore density of 10^8 pores/ cm^2 and pore diameter of 100 nm were selected for this experiment.

The electrochemical cell, fabricated in our laboratory using Perspex sheets, was washed in double distilled water. A copper rod of 0.3 cm diameter was used as a sacrificial electrode (anode). The cathode consists of copper foil attached to alumina disc by an adhesive tape of good conductivity. The electrolyte used had a composition of 20 gm/100ml $CuSO_4.5H_2O$ + 25% of dilute H_2SO_4 at room temperature. The inter-electode distance was kept 0.5 cm and a current of 2mA was applied for 10 minutes. The anodisc was kept immersed in 1 M NaOH for 3 hours in a beaker to dissolve alumina template. The copper nanowires were liberated from the host matrix, washed in distilled water and dried in an oven at 50^0C for 30 minutes. The cleaned and dried nanowires were mounted on aluminium stubs with the help of double adhesive tape, sputtered with a layer of gold using Jeol sputter JFC 1100. Scanning electron microscope (Jeol, JSM 6100) was used to record cross-sectional and lateral views of grown nanowires at an accelerating voltage of 20kV using different magnifications. The images of copper nanowires were recorded on the photographic film in the form of negatives and developed in a dark room.

Experiment was repeated using polycarbonate membranes as templates and keeping the other conditions identical. The polymer template was dissolved in dichloromethane to liberate copper nanowires from the host matrix. The rest of the procedure is same. Polycarbonate membrane with pore diameter of 20 nm was also selected for growth of copper nanowires but the results were not quite satisfactory.

Results and Discussion

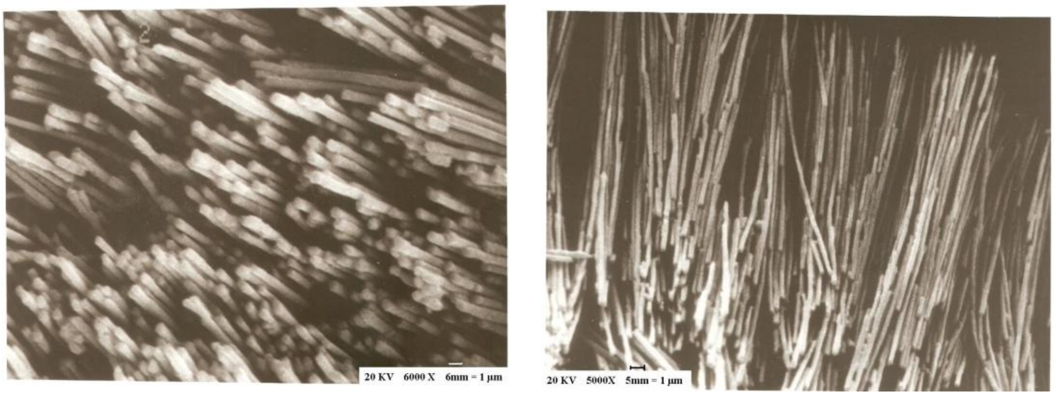
Atomic force microscopic technique [7] shows the two dimensional surface topology of the anodic alumina template with hexagonal pores regularly arranged on the surface. The pores appear nearly at the centre of each hexagonal cell (Fig. 1a). After gold sputtering, the SEM micrograph (Fig. 1b) shows the geometrical pattern of pores on the aluminium surface of anodisc.



(a) (b)

Fig. 1(a) AFM image of hexagonal pores (b) SEM micrograph of anodisc pores

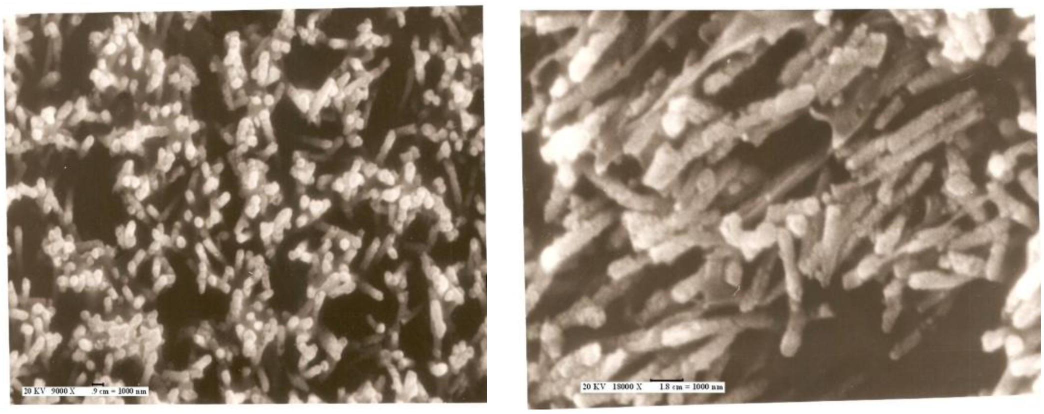
Electrodeposition of copper nanowires depends on many factors, namely, inter-electrode spacing, electrolyte composition and pH value, current density and time of deposition. To achieve uniform deposition of nanowires, templates were cleaned in the ultrasonic bath for 10 minutes. After cleaning, the templates were fixed to the adhesive copper tape to make it a perfect cathode. Copper nanowires were examined under SEM under different magnifications. Fig. 2 (a) shows a typical cross-sectional view of copper nanowires grown in alumina template. Fig.2 (b) represents the lateral view of nanowires. Obviously, the diameter of copper nanowires is identical to the diameter of pores (200 nm) of anodisc. Nanowires are quite uniform but they are not perfect cylinders. It has been reported [8] that pore diameters of commercially available templates vary over a large range. The aspect ratio, that is, the ratio of length to diameter, is on the order of 300.



(a) (b)

Fig. 2(a,b) SEM images of Copper nanowires (cross-sectional & lateral views)

Electrodeposition of copper nanowires was achieved in polycarbonate template under identical conditions. The polymer template was dissolved in dichloromethane at room temperature. SEM micrographs of grown copper nanowires are shown in Fig. 3(a,b). The cross-sectional and lateral views are somewhat distorted and not as smooth as in case of anodisc alumina templates. The diameter of copper nanowires matches with the pore diameter (100 nm) of polycarbonate template.



(a) (b)

Fig. 3(a,b) SEM images of Copper nanowires (cross-sectional & lateral views)

We repeated the experiment for 100 and 20nm pore diameter anodisc templates. Due to overdeposition of copper into pores, we failed to grow copper nanowires. Instead, what we achieved was quite interesting. SEM micrographs (Fig. 4) show copper nanocrystals of various shapes and sizes. Another interesting feature (Fig. 5) was a flower pattern resembling nature's self assembly. It is reported [9] that overdeposition of copper may also lead to metallic micro-rose having petals in nanometer dimensions.

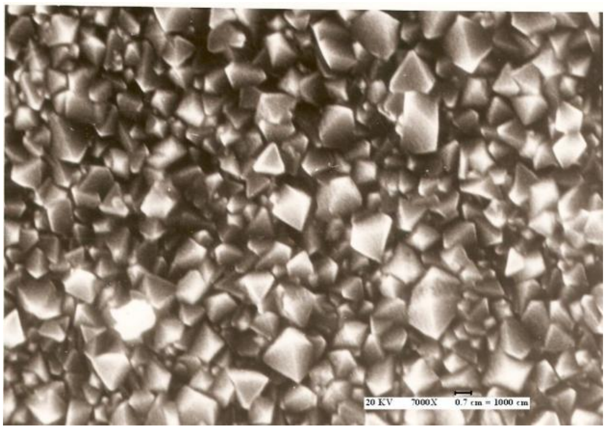


Fig. 4 SEM micrograph of Copper Nanocrystals.

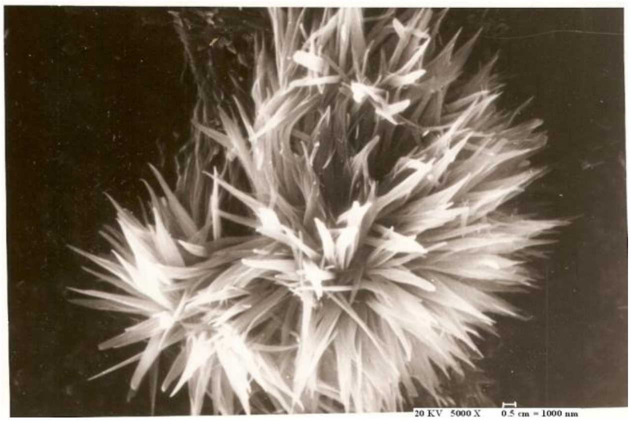


Fig.5 SEM micrograph showing some flower pattern due to over-deposition.

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