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Preparation and Structural Characterization of Template Assisted Electrodeposited Copper Nanowires

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Metallic nanowires have potential applications in miniaturized metallic interconnects, sensors and heat sink materials. In this work, highly aligned amorphous copper nanowires have been prepared by electrodeposition technique using anodized aluminium oxide (AAO) templates at room temperature. FESEM analysis shows that the as-deposited nanowires are parallel to one another and have high aspect ratio with a reasonably high pore-filing factor. The electrolyte used, consisted of a bath solution containing $CuCl_2.6H_2O$ buffered with H_3BO_3 and acidified by dilute H_2SO_4. To fabricate the working electrode, a thin film of aluminum (~ 152 nm thick) was coated on back side of AAO template by e-beam evaporation system to create electrical contact. During the electrodeposition process, the copper ions were guided to move through nano-pores where they were reduced to form one dimensional structure of pure copper nanowires. The lengths of deposited nanowires could be controlled by deposition time, applied voltage, composition of precursors. The electrodeposited nanowires have diameter varying from 15-200 nm. TEM results show that the as-deposited nanowires were dominantly amorphous with small portion of crystalline structure.

Keywords: Anodized Aluminium Oxide (AAO), electrodeposition, metallic interconnects, miniaturized, nanowires

1. INTRODUCTION

Recently, nanowire structures have attracted immense attention because of their quantum confined directions and unique chemical and physical properties [1, 2]. The most important factor, in the fabrication of these one dimensional nanostructures, is the control on composition and structure. It is generally accepted that in this kind of nano structure, chemical and physical behaviour are dominated by structural properties like length, diameter and morphology [3]. Metal nanowires have been widely studied for application in semiconductor devices and Micro Electro-Mechanical System (MEMS) elements. Nanowires of metallic materials such as copper nickel, iron, cobalt, and their alloys are one of the most widely investigated structures because of their possible applications in heat sink, metallic interconnects, high density magnetic recording media, sensor elements and building blocks in biological transport systems [4-8]. The formal fabrication techniques used are physical vapour deposition, chemical vapour deposition, and electrodeposition. Electroplating has achieved a special interest because of the unparalleled advantages such as low production cost, high purity of the products, and high throughput. One of the simplest methods to fabricate metal nano-structures using electroplating is the so-called template-assisted electroplating which makes use of porous membrane such as anodized aluminium oxide (AAO) disk, polycarbonate filter membrane, and di-block copolymer. This method is cost effective and can be used for mass production of nanowires with controlled geometry and morphology [9-11]. Among templates, AAO templates are the most widely used for nanowires deposition. These templates have advantage to precisely control the diameter of nanowires, as the diameter is dictated by the pore size of the nano-channels of AAO templates [12-14].

The objective of this work was to prepare Cu nanowires by using template assisted electrodeposition and to achieve nanowires with fine structure, reasonable pore filling factor and aspect ratio, high purity and highly parallel copper nanowires at room temperature.

2. EXPERIMENTAL

In this work, commercial AAO templates used were obtained from Whatman Company (Maidstone, Kent, UK, Product ID No. 6809-6002). One side of anodized aluminum oxide (AAO) template was first coated with aluminum (Al) by e-beam physical vapor deposition method (e-beam PVD) to act as cathode during deposition of copper nanowires. The AAO template was coated using NanoFilm Technologies International PTE LTD (NTI-2004) e-beam evaporation system under vacuum. The thickness of the coated film was around 152 nm as shown in figure 2 (b).

Standard solution of Reagents containing chloride salt of copper was prepared with controlled pH and molarity. The pH of the solution was adjusted to 3 and molarity was fixed to 0.1 M by using dilute H_2SO_4 and buffered by 0.2 M H_3BO_3 to increase the plating life of bath. The deposition of the copper nanowires was carried out by using typical electrodeposition bath technique where the anode is a pure copper wire of 1mm diameter and aluminum coated template acted as the cathode.

The Schematic diagram of the deposition bath used for the electrodeposition of copper nanowires is shown in the figure 1. The anode in the bath consisted of pure copper metal wire indicated by positive sign while, for the cathode, the e-beam deposited thin film of aluminum serves the purpose. At the back of thin conducting aluminum film there is supporting copper sheet of 1mm thickness which supports and provides electrical current to the cathode. To avoid deposition at the back side of thin copper an adhesive insulated tape was used. This deposition bath was then interfaced to computer to control and record the electrical parameters like current density during the deposition process. As a result of electrodeposition, the copper ions moved into the nano-pores of templates where they were reduced to copper metal and the nanowires started developing as shown in figure by blue color.

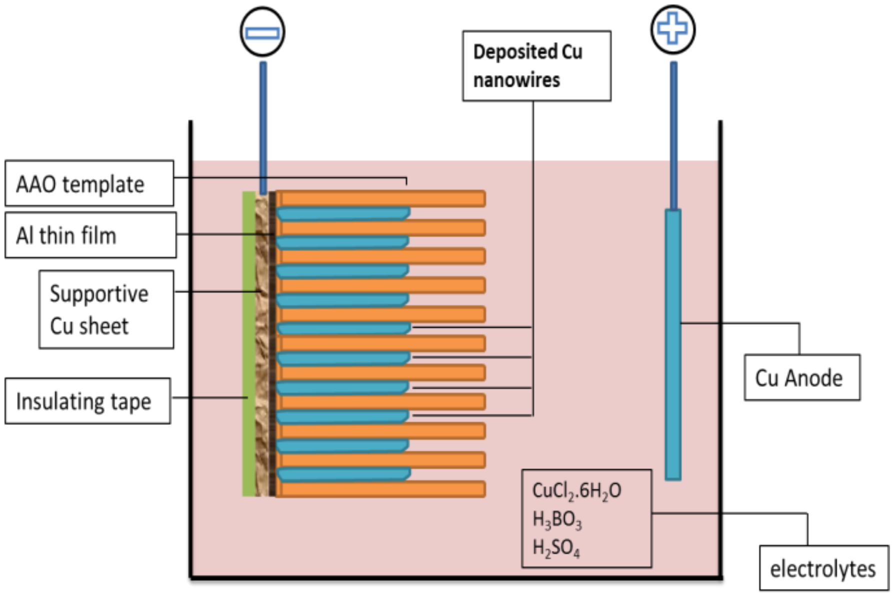

Figure 1. schematic diagram of electrodeposition bath for Cu nanowires

The SEM image of pore size before deposition and its distribution across the template is shown in figure 2 (a). The pore diameter varies in the range of 15-200 nm. However, minimum value of the pore size found is around 15 nm and the average diameter is around 40 nm.

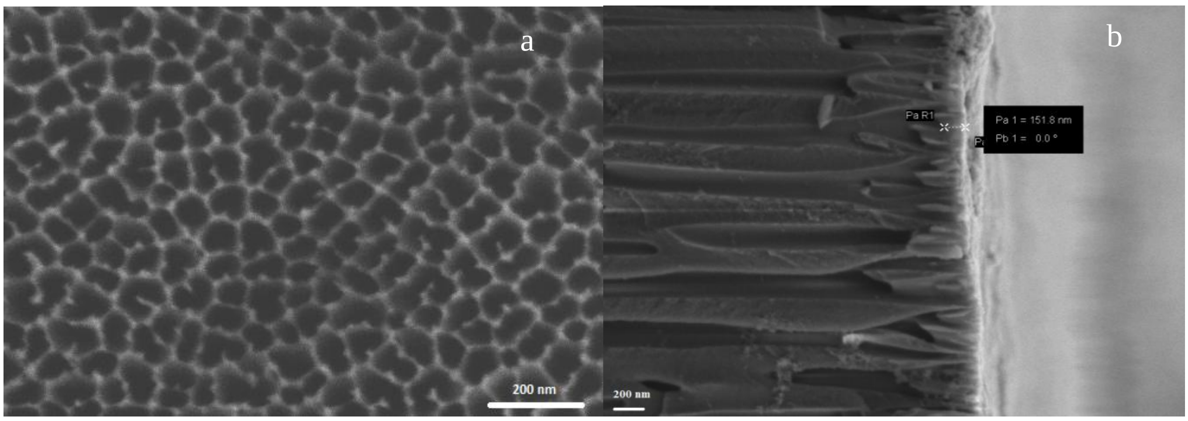

Figure 2. (a, b). (a) SEM images of AAO template before deposition (b) thickness of deposited aluminium thin film

A schematic diagram showing thin film coating, electrodeposition of nanowires, removal of templates and free nanowires is given figure 3 (a, b, c, d).

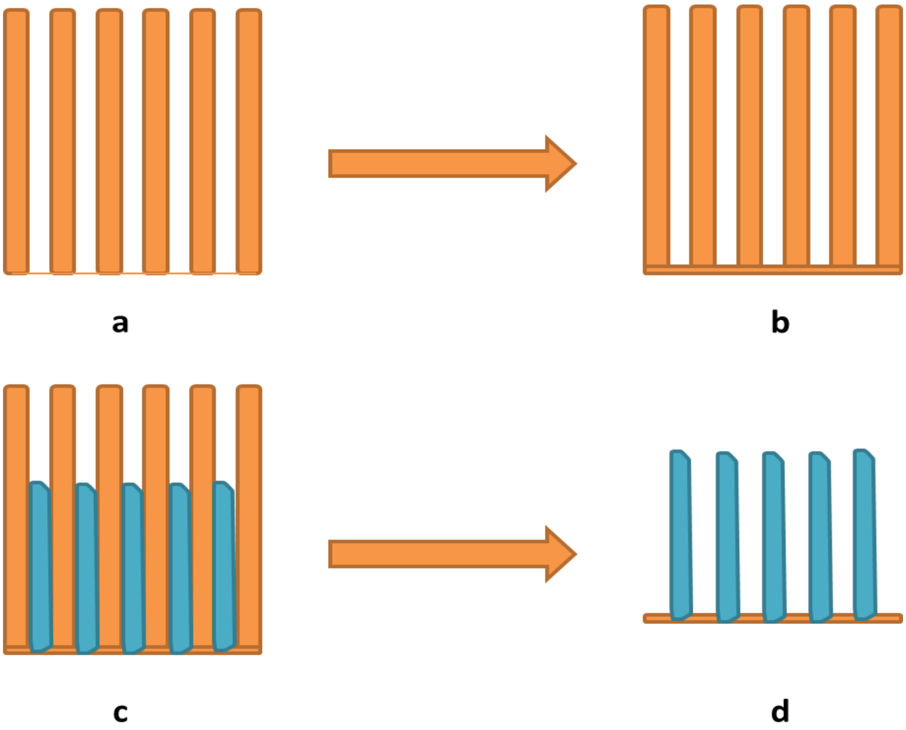

Figure 3. A schematic diagram of template filling and removal process; (a) AAO template (b) thin film coated AAO template (c) electrodeposition of AAO template (d) free nanowires after removal of AAO template

A Carl Zeiss (Supra 55VP-2009) field emission scanning electron microscope (FESEM) and a Carl Zeiss (Libra 200 FE-2009) transmission electron microscope (TEM) was used for morphological study.

3. RESULTS AND DISCUSSION

The current density profile graph during the deposition of copper nanowires is shown in the figure 4. To understand the growth mechanism of nanowires, the current density profile data curve can be divided into three parts indicated as by arrows. In the beginning, the current density increases which show that all the pores were empty. After an approximate interval of 12 minutes, as in the second region of curve, the pore-filling factor increases leading to an increase in the current density. However, the current density becomes almost constant in the third region after 50 minutes. This is attributed to the growth of nanowires that proceeds on to the whole template surface. This value represents the current measured on a metallic electrode of the same surface area and for the same applied voltage which is -1.8 V [15, 16].

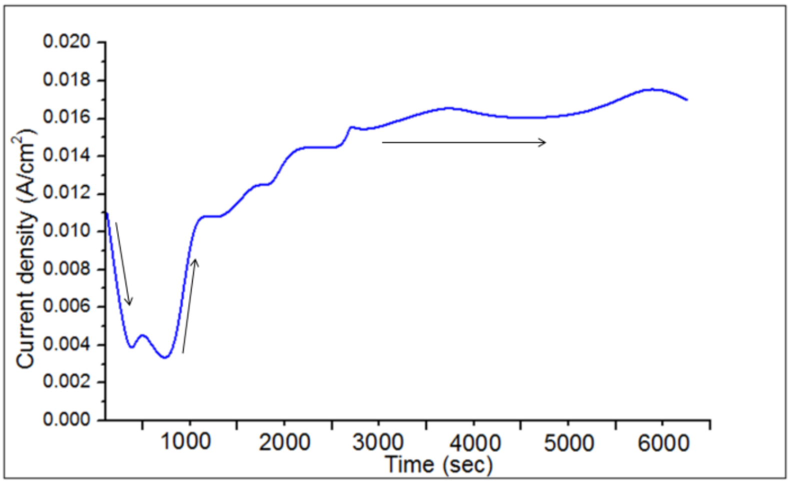

Figure 4. current density variation versus time during the electrodeposition of Cu nanowires

Field emission scanning electron microscopy (FESEM) was used for surface morphology and EDX for compositional analysis. For imaging, one of the templates was sacrificed by breaking from the middle and viewed from the cross section as shown in figures 5(a, b). In SEM images, it was observed that the deposited Cu nanowires are aligned parallel to each other and length is ranging 20-25 μm and exhibited high aspect ratio. The pore-filling factor achieved in this electrodeposition process is also reasonable. The surface morphology reveals that particles are well bound together in nanowires and do not have broken or shattered portions which suggested that the nanowires are of good quality [17].

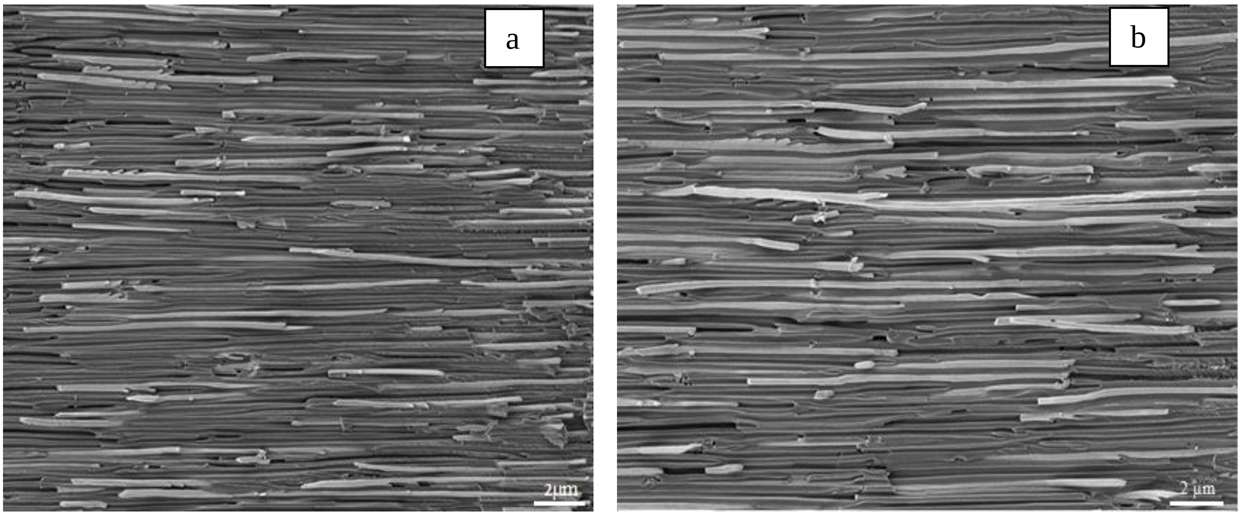

Figure 5. (a, b). SEM image of electrodeposited Cu nanowires

The elemental composition was found by energy dispersive X-Ray spectroscopy (EDX) and the atomic percentage of Cu was around 24 % as shown in figure 6.

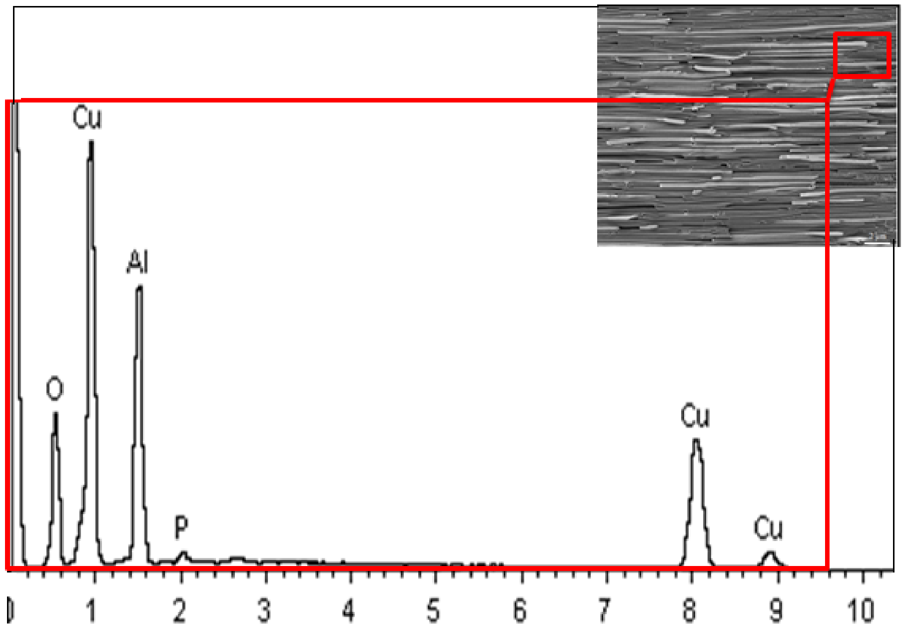

Figure 6. EDX shows the presence of Cu

In the EDX results, aluminum and oxygen are present due to template composition which consists of Al_2O_3. There is also some percentage of phosphorus. The presence of phosphorus was due to the use of phosphoric acid (H_3PO_4) in template preparation for successive anodization of the aluminum film.

The detailed investigation of the nanowire structure was done using transmission electron microscopy (TEM). The TEM sample was prepared by dissolving the template in 1M NaOH solution at 60 °C for two hours. The NaOH solution was removed by pouring de-ionized water slowly and taking out with a dropper. The sample was then sonicated for 30 minutes and specimen was then put on a copper grid for TEM analysis.

The TEM images show that the minimum diameter of nanowires is around 15 nm. This is due to the fact that in the solvent, the nanowires with small diameter and less weight are more probable to be taken out as they do not settle down at the bottom compared to heavy nanowires with larger diameter and weight. The wires have amorphous and crystalline mixed structure which can be distinguished easily by looking at the fringes portion. At boundaries and middle portion the structure is mostly amorphous. However, between the outer layer and central part, there are some well-defined walls showing the crystalline portion as shown in figure 7(a, b).

The TEM images give a more clear insight into the internal structure of nanowires. It can be observed in figure 7 (b) that the nanowires have both crystalline (shown in enlarged rectangle) and amorphous phases with a majority of amorphous portion. The outer and central portion of the nanowires is amorphous. However, in between there is some crystalline portion. This is attributed to the deposition of the ions which started on the walls of alumina (Al_2O_3) nano-pore where there is lattice mismatching for a few layers of the deposited copper but with the successive layers of the same material, the crystalline structure was developed. In the central portion, due to the deposition of copper material on the walls of the pore, the incoming copper ions do not have sufficient time and the pore is not wide enough to accommodate the incoming ions in a particular orientation. The second possible reason could be due to applied potential. In this work, higher applied potential around -1.8 V was used. The higher potential leads to the formation of polycrystalline and amorphous structure [18-22].

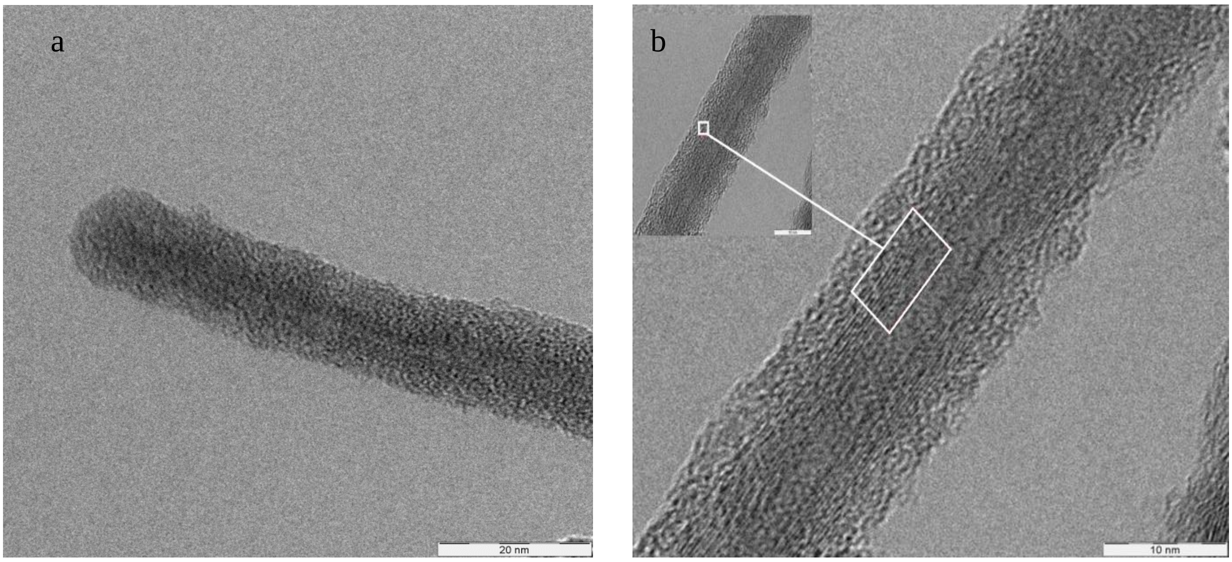

Figure 7. (a, b). TEM images of Cu nanowires

The electrodeposited Cu nanowires have great potential to be used for nano-structured systems such as MEMS devices, sensing elements, and also as an alternative of metallic interconnect in miniaturized devices [23].

4. CONCLUSION

In this work, electrochemical synthesis of metallic copper nanowires assisted with anodized aluminium oxide templates (AAO) in a simple bath containing chloride salt of copper, was studied. The nanowires deposited were aligned parallel to each other, having high aspect ratio and have reasonably high pore-filling factor .It was possible to deposit nanowires with as small diameter as 15 nm using comparatively low cost technique of electrodeposition. The structural properties show that deposition at a higher potential leads to the formation of dominantly amorphous structure. The metallic copper nanowires with large surface area are suitable to be used in applications like ohmic contacts between different parts of nano-devices, sensors and heat sink composite materials.

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