World Academy of Science, Engineering and Technology
International Journal of Electronics and Communication Engineering
Vol:6, No:7, 2012

Synthesis and Characterization of Cu-NanoWire Arrays by EMD Using ITO-Template

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Abstract—Nanowire arrays of copper with uniform diameters have been synthesized by potentiostatic electrochemical metal deposition (EMD) of copper sulphate and potassium chloride solution within the nano-channels of porous Indium-Tin Oxide (ITO), also known as Tin doped Indium Oxide templates. The nanowires developed were fairly continuous with diameters ranging from 110-140 nm along the entire length. Single as well as poly-crystalline copper wires have been prepared by application of appropriate potential during the EMD process. Scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), small angle electron diffraction (SAED) and atomic force microscopy (AFM) were used to characterize the synthesized nano wires at room temperature. The electrochemical response of synthesized products was evaluated by cyclic voltammetry while surface energy analysis was carried out using a Goniometer.

Keywords—Electro-deposition, Metallic nano-wires, Nano-materials, Template synthesis

I. Introduction

METALLIC nanowires have tremendous potential to revolutionize research in diverse fields like chemistry, optics, electronics, medicine and others as they exhibit unique electrical, optical, mechanical and magnetic properties. Low dimensional nanowires exhibit unique properties due to their shape, size and intra-atomic and inter-molecular interactions.

While Tseng et. al. [1] and Cao [2] have reported the use of nanowires as interconnects in nanometer-scale electronics, Azarian et. al. [3] have emphasized the importance of Cu-nanowires in the microelectronics industry due to their high electrical conductance, thus exhibiting significant applications as sensors [4]-[9], fuel cells [10], electrical devices [11]-[12] and catalysis [13]. In the past decade, several studies have been published on the synthesis of single-crystal metal nanowires of Cu, Ag, Au and Ni [14]-[17].

Even though several methods like electrochemical reactions [18]-[23], vapour deposition [24]-[25], soft and hard template processes [26]-[27] and reverse micellar systems [28] - [31] have been developed, majority of them suffer from intrinsic drawbacks in maintaining control over morphology of the structures.

Anodized Aluminium Oxide templates have been widely used for nanowire synthesis. This methodology, however, suffers from an inherent drawback of nonlinear morphology, poly-dispersivity, poor crystalinity, low yield, and process complexity. While Lin. et. al. [17] have demonstrated ordered preparation of nano rod arrays on AAO membranes, they could not achieve uniform growth of nanowires because of nonavailability of finer AAO templates, thereby leading to poor crystalinity and non linear morphology. Burdick et. al. [32] have observed that synthesis by AAO technique used only a very small portion of the porous template thickness thereby resulting in low yield. Further in [13] AAO templates have been reported to be unstable at pH >11. These observations limit the utility of the AAO template for synthesis of nanowires and hence serve as motivation behind the current research. This paper, reports the synthesis of arrays of copper nanowires using ITO (Indium-Tin oxide) templategrowth electrochemical deposition method on a flat ITO coated glass plate as the working electrode.

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II. Experiment

Potentiostatic EMD technique was utilized for synthesizing the Cu nanowires using a flat ITO coated glass plate as the working electrode. Thin Pt wire was used as a counter electrode and Ag/Agcl used as a reference electrode in the sample cell shown in Fig. 1. The system comprises of a conventional 3-electrode bath containing a mixture of 0.025% $CuSO_4.5H_2O$ and 0.15% KCl. The pH of the solution was maintained at 4.5 by adding 0.1 M H_2SO_4.

Electrochemical deposition of Cu was carried out at the room temperature for 3-4 hours by applying constant voltage levels. Tests were conducted for three voltage levels namely; -0.15V, -0.30V and -0.45 V in a CHI-604D electrochemical analyser. After the process was over, the ITO plate was removed from the cell and cleaned using organic solvents. Final cleaning was performed with de-ionized H_2O to remove any adhering copper particles. The sample surface was subsequently dried under a constant stream of clean air and used for further characterization.

Scanning electron microscopy (SEM) of the nanowires was carried out with the help of JEOL JSM-6360. Scanning electron microscope uses low energy secondary electron or high energy back scattered electron from the specimen surface for image formation and provides valuable information regarding the structural arrangement, spatial distribution, wire density, and geometrical features of the nanowires. A cut section of the template was taken and it was electroplated using Au sputtering electroplating equipment. Au electroplating is needed for making the template highly conducting and also to prevent the disturbances native to SEM experimental setup. Sample prepa-

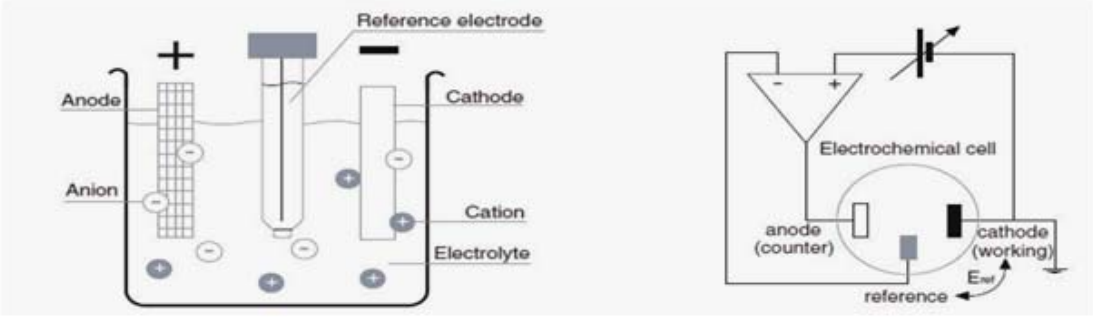

Fig. 1. The electrode setup used for EMD through template growth for Cu-nanowire

ration for Transmission electron microscopy (TEM) (JEM-2100) and Small angle electron diffraction (SAED) analysis was carried out by taking a cut section of the ITO template containing the copper wires and dissolving it in ethanol and distilled water respectively. The sample was sonicated for 30 minutes at room temperature under high frequency of 54 KHz to de-agglomerate the nanowires which may otherwise lead to high degree of clustering, which was followed by loading a suitable volume of the sample on a copper grid. The copper grid was then kept inside an oven at 303.15 K to remove the moisture on the sample in the grid.

The grid was then placed in the grid holder of TEM gun and at high voltage of 200 KV, the characteristics of the sample were studied. Small angle electron diffraction pattern of the samples were obtained using high resolution TEM at the camera length of 80 mm. The contact angle and thereby the surface energy of the sample was measured using video contact angle system (VCA OPTIMA-XE). A drop of the sample was placed on the surface of a solid using goniometer. The correlation of contact angle data with surface tension provided the fundamental information for critical surface analysis for the nanowire samples.

While the surface morphology of the ITO plate and copper nanowires was determined with nanosurf easy-scan 2 atomic force microscopy (AFM), video camera in dynamic mode, the conductivity properties of the sample were determined with the CHI electrochemical analyser using cyclic voltammetry, linear sweep voltammetry, onoamperometry, chronocoulometry, bulk electrolysis and AC impedance. Variation of open circuit potential against time was measured to generate the TAFEL plot of the sample. The generated data was subjected to regression analysis in order to study the characterization of the metallic nanowires.

III. Result and Discussion

Successful synthesis of straight singlecrystalline copper wires with face centred cubic structure using EMD on ITO glass template was performed. Results attained show greater uniformity, higher yield and low development time as compared to the AAO template technique.

Cu NW arrays were grown on ITO glass (123nm pore channel size) template with the help of an electric field using electrochemical deposition technique. The applied initial voltage was -0.3 V and the deposition lasted for three hours. Upon the completion of deposition, the samples were dried for more than 12 hours to ensure complete dryness. They were then immersed in organic solvent and the de-ionized water for 30 minutes to dissolve the ITO plate. The sample was then subjected to various characterization techniques for investigation.

Scanning electron microscopy of the copper nanowires grown on ITO template revealed typical cylindrical structures ranging in diameter from 110 nm to 140 nm and length of 5296 nm as shown in Fig. 2.

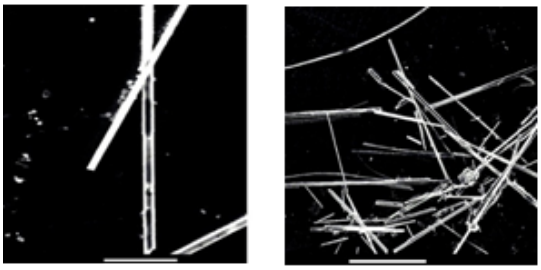

Fig. 2. SEM images of copper nano wires. (bars: 1 μm)

SEM image in Fig. 3(a) depicts uniformity of the nanowire lengths. The accurate determination of diameters is difficult due to the small lateral distance between the nanowires. Gao et. al. [19] have, however, reported an average length of 30μm and an average diameter of 60nm for Cu nanowires synthesized by ECD on PAA template. Our results, however, indicate that EMD on ITO template can be used to generate smooth cylindrical and uniform nanowires of Cu. Fig. 3(b) shows the topographic image of an ITO coated glass template taken with the help of AFM. It demonstrates the corresponding dimension of each nano pores in the template. The pore size as obtained from the images comes to be approximately 123nm.

The morphological and Structural analysis of the copper nanowire was performed by HR- TEM techniques. Fig.4(a) shows continuous and free ended individual copper nanowires with diameter observed to be around 35.69 nm on an average. The electron micrograph snapshot as shown in Fig.4(b) suggests a uniform and uninterrupted wire structure for the copper array, where no segmentation or morphological imperfections, such as branching is observed.

The crystalline structure of nanowires was investigated by

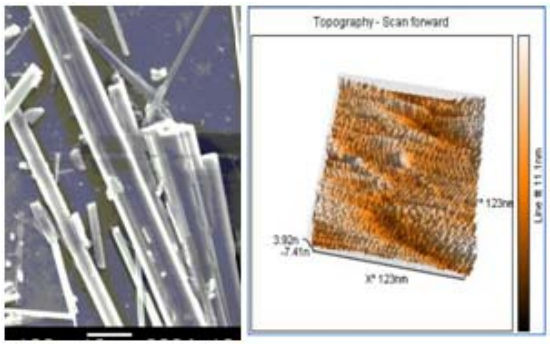

Fig. 3. (a) SEM image of Copper nanowires showing uniformity of lengths and cylindrical shape. (b) AMF photograph showing the pore size of ITO template

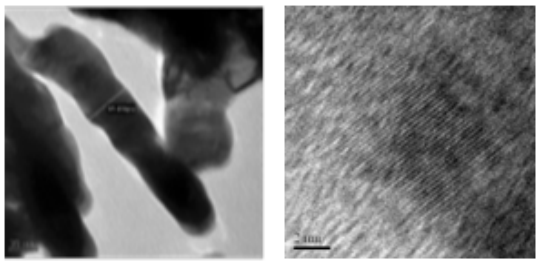

Fig. 4. (a) TEM image of continuous and free ended Cu nanowire taken. (b) TEM image of uniform and uninterrupted wire structure for the copper array

the SAED technique and individual copper nanowires were used for characterization. Fig. 5 shows the SAED patterns of the Cu nanowires. Many individual copper nanowires were characterized and we always observed a single set of diffraction spots in the SAED patterns, indicating that the copper nanowires were single crystalline with an fcc structure. The results reveal that Cu nanowires can be predictably synthesized as either a single crystal or polycrystalline structure at a specified suitable applied potentials in the potentiostatic EMD process.

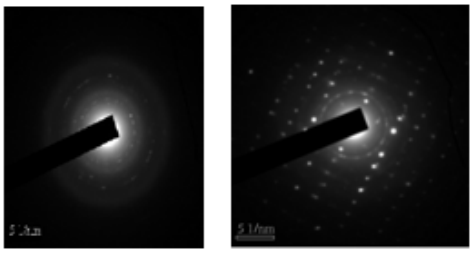

Fig. 5. SAED patterns, indicating that the copper nanowires were (a) single crystalline and (b) fcc structure

The electrochemical synthesis experiments were controlled by Electrochemical analyser (CHI 604D). The counter electrode, along with the working electrode, provided a circuit over which current was either applied or measured and hence electrical properties of the nanowires were measured. The potential of the counter electrode was usually adjusted so as to balance the reaction occurring at the working electrode. This configuration allowed the potential of the working electrode to be measured against a known reference electrode without compromising the stability of the reference electrode by passing current.

Using bulk electrolysis technique in the CHI Electrochemical analyser, the variation of charge against time has been studied. Fig. 6 shows that the charge on electrode is directly proportional to time during which the deposition of nano particles takes place into the available pores on the template leading to the growth of the nanowire. Cu^2+ in the solution of $CuSO_4$ and KCl was reduced to Cu till equilibrium was attained and then deposited atom by atom on the conducting surface of the ITO coated glass template (working electrode). The total Q observed from Fig. 6 is 9.8880e+0C with an Initial E (V) = - 0.3V. The electrical properties of nanowires

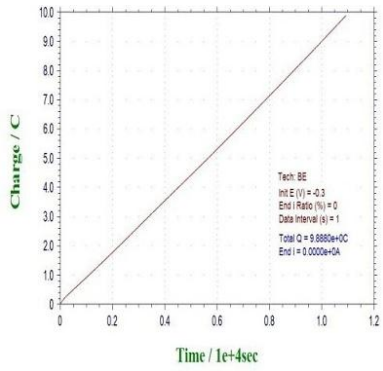

Fig. 6. Variation of charge against time during synthesis of copper nanowires

synthesized were studied using Sweep and A.C techniques. For cyclic voltammetric study, the electrode was subjected to following constraints:

- Initial limit of potential scan = -0.3V
- Upper limit of potential scan = +0.6V

The initial scan direction was taken as positive.

- Potential scan rate (V/s) = 0.1
- Sweep segment = 2
- Data sample interval(V) = 0.001
- Quiescent time before potential scan (sec) = 2
- Sensitivity scale (A/V) = 1e-6
- Ep, ip and An = 0.237 V, 6.696e-6 A and 2,720e-6 C respectively.
  Fig.7 represents :
- E = l 0.0720 V
- I = 4.854e-6 A.

With these parameters, the results obtained from Fig.7 exhibit a peak around 0.5V, indicating that V has efficiently accumulated on the surface of the electrode. This elevation in the current therefore may be caused by the growth in the nano wires [34]. Fig.8 shows the potential wave form applied as a function of time. The current is recorded as a function of potential using linear sweep voltammetry. From Fig. 8,

- E = -0.1274 V
- I = 9.768e-6 A.

Fig. 9 exhibits the TAFEL plot, where potential is scanned from Initial E towards the final E. The logarithm of current is recorded as a function of potential. From Fig. 9,

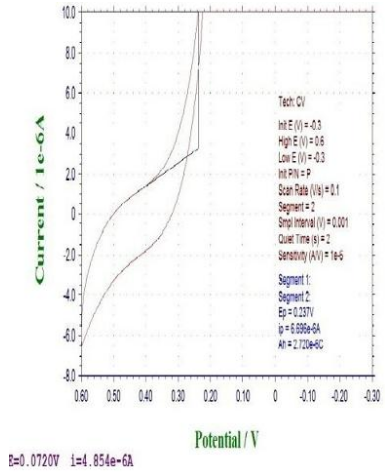

Fig. 7. Variation in Current as a function of applied potential in the synthesized copper nanowires

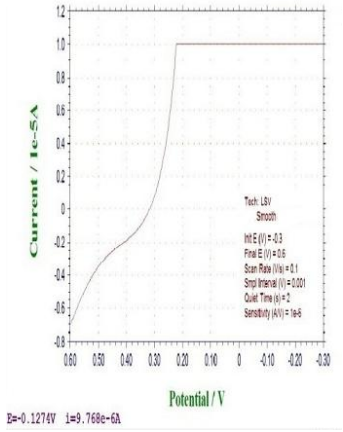

Fig. 8. Variation in potential wave form applied as a function of time

- E = -0.1595 V
- log(1/A) = -7.4004

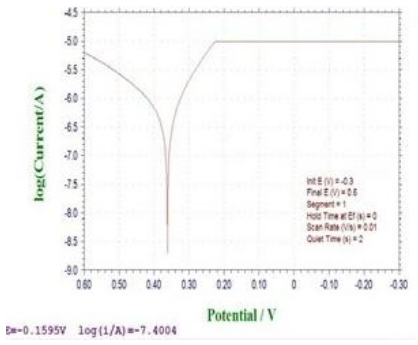

Fig. 9. Tafel plot showing variation of log (current) against the applied potential in the synthesized copper nanowires

The impedancetime variation, (IMPT) shown in Fig.10 has constant base potential at Initial E = -0.3 V. A sine wave is super imposed to the base potential. The current and the potential are sampled and analyzed to obtain the real and imaginary impedance. The dependence is recorded as a

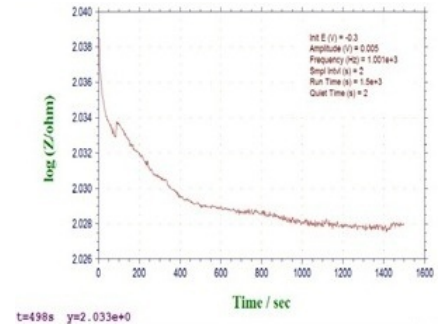

Fig. 10. Variation in impedance as a function of time (IMPT) of the synthesized copper nanowires

function of time.

- Amplitude (v) = 0.005
- Frequency (Hz) =1.001e+3,
- Time (t) = 498s
- Output (y) = 2.033e+0

In case of AC impedance (IMP), the frequency is scanned from high to low frequency with log Z(ohm) and phase(deg.) as shown in Fig. 11 and Fig. 12. The nonlinear IV character-

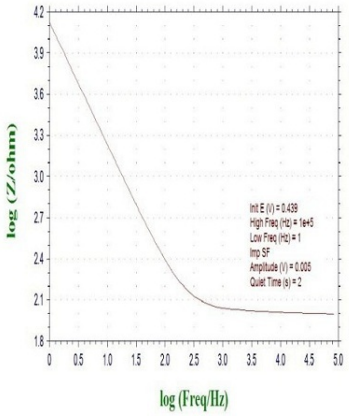

Fig. 11. Variation in impedance as a function of frequency in the synthesized copper nanowire

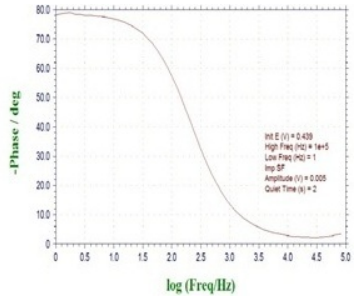

Fig. 12. Relationship between phase deg^{-}1 vs log Freq Hz^{-}1 in the synthesized copper nanowires

istic of the synthesized copper nanowire arrays suggests the presence of a potential barrier. The measured contact angles of the samples are reported in Fig.13. Surface tension of solution before synthesis was 65 dyne/cm while after the synthesis

Fig. 13. Surface tension of the solution used for synthesis of copper nanowires (a) before and (b)after the synthesis

it was 61.26 dynes/cm. The decrease in the surface energy property indicates that the adhesive forces are being transferred to the formed nanowires increasing its magnetic properties.

IV. Conclusion

Our investigations confirm that electro-deposition of copper nanowires on Indium tin oxide (ITO) template is the simplest route to the synthesis of copper nano wires. The template based electro-deposition technique is actually the most cost effective way to generate nano structure on ITO template. The 3 hours preparation time of nanowire arrays is quite short in comparison to AAO template technique preparation time. The synthesized Cu Nanowires were of uniform diameter. The synthesis revealed formation of bulk production of nano wires over complete area of ITO plate in contrast to AAO templates.

Copper nanowires reveal effect of high current density resulting in over deposition in the form of bulk growth and not as perfect cylinders. Over-deposition results in growth of copper buds which may need to be avoided. The aspect ratio being very high, of the order of 300, the copper nanowires may be used as field emitters. I-V characteristics do not confirm to normal p-n junction behaviour and may need further investigation. The nonlinear IV characteristics of the synthesized copper nanowire arrays suggests the presence of a potential barrier.

Additionally, it was observed that there were no obvious differences between the morphologies of the individual copper nanowires formed at different applied potentials (0.15, 0.30, and 0.45 V,) because ITO templates with the same geometrical characteristics were used in every case. The diameter distribution of the wires was obtained from statistical results for 20 wire diameters through the TEM images, thereby revealing that the diameters of Cu Nanowires were 100nm and above, while some were even below 50nm and hence seemed to be in good agreement with the ITO Template.

Acknowledgment

The authors thank Director, SAIF North Eastern Hill University, Shillong, Meghalaya, India for providing necessary SEM and TEM facilities.

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