Journal of NanoScience, Nanoengineering & Applications
Volume 1, Issue 1, February, 2011, Pages 1-16.

Fabrication and Characterization of Copper Nanowires: An Overview

Hardev Singh Virk

Nanotechnology Laboratory, DAV Institute of Engineering & Technology,
Kabir Nagar, Jalandhar, India

ABSTRACT

Copper (Cu) 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 200 nm using Anodic Alumina and polymer membranes as templates. Template-based growth of copper nanowires has been realized using conventional electro deposition technique in an electrochemical cell designed in our laboratory. Fabrication of copper nanowires is one of the most important thrust areas of nanotechnology because of their potential use in the micro/nanoelectronics industry and, in particular, for interconnection in electronic circuits. Many methods have been developed for the fabrication of copper nanowires but template synthesis is considered to be the 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).

Scanning Electron Microscope (SEM) is used to calculate the aspect ratio of nanowires. Field Emission Scanning Electron Microscope (FESEM) images and Energy Dispersive X-ray Analysis (EDX) reveal morphology and chemical composition of fabricated nanowires. The morphology of nanowires shows some interesting features. X-ray diffraction (XRD) spectrum reveals crystalline nature of Cu nanowires with crystallite size of 1.12 nm. During our experiments, we observed that when we failed to fabricate nanowires in polymer templates, what we got was some exotic patterns of metallic copper in the shape of copper buds and flowers on the cathode surface. There is as yet no specific theory to explain exotic patterns developed during electrodeposition of copper in anodic alumina or polymer templates. It is speculated that overdeposition of copper results in formation of exotic patterns.

Keywords: Electrodeposition, Anodic alumina membrane, Cu nanowires, nanoflowers and nanobuds, Polycrystalline Cu crystals, XRD.

Author for Correspondence Email: hardevsingh.virk@gmail.com; Cell Phone: 91-9417553347; Fax: 91-181-2205852

Journal of NanoScience, Nanoengineering & Applications
Volume 1, Issue 1, February, 2011, Pages 1-16.

1. Introduction

Synthesis, characterization and application of nanowires and nanotubes comprise a significant aspect of today's endeavor in nanotechnology. 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 [1-3]. 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].

Template-based growth is a versatile method of synthesis of metallic and semiconductor nanowires. Many studies have focused on the fabrication of copper nanowires [4-8], because of their potential applications in the micro/nanoelectronics industry and, in particular, for interconnection in electronic circuits. A recent study [9] has established that copper nanowires could revolutionize the development and production of low-cost flexible displays, light emitting diodes and thin film solar cells. Copper is one of the most important metals in modern electronic technology. Copper is 1000 times more abundant than indium or silver, and is 100 times less expensive. As a consequence, films of copper nanowires represent a low-cost alternative to silver nanowires or indium tin oxide (ITO) for use as a transparent electrode.

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 [1], namely, pulsed laser deposition (PLD), vapour-liquid-solid (VLS) method and chemical vapour deposition (CVD). 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 Field Emission Scanning Electron Microscopy (FESEM). The diameter of nanowires generally depends upon the pore size of template. Anodic alumina discs of 200 nm and polymer membranes of 100 nm pore diameter were selected for this purpose.

Template materials must meet certain requirements [4]. First, the template materials must be compatible with the processing conditions. For example, an electrical insulator is required for a template to be used in electrochemical deposition. Template materials should be chemically and thermally inert during the synthesis. Secondly, depositing materials or solution must wet the internal pore walls. Thirdly, for synthesis of nanowires, the deposition should start from the bottom of the template and proceed upwards to the other side. This is known as bottom up technique in nanotechnology.

Template-based synthesis offers many advantages over other methods of synthesis [10]: (1) It is performed under mild conditions rather than requiring high temperatures, high vacuum or expensive instrumentation; (2) templated electro-deposition has a relatively high growth rate; (3) the morphology of deposited materials depends on the shape of template pores; (4) the dimensions of the materials obtained can be tuned by tuning of the template pore size; (5) two or more components can be easily deposited into the membrane sequentially to form multi-segmented materials or hetero-junctions.

2. Materials and Methods

The electro-deposition technique used in our experiment [11] is similar in principle to that used for the electroplating process. Commercial anodic alumina membranes (AAM) (anodisc 25 made by Whatman) having an average pore diameter of 200 nm, a nominal thickness of 60 μm and a pore density of 10^9 pores/ cm^2, were used as templates. A second set of experiments was performed using polymer membranes (Sterlitech USA) of 100 nm and 20 nm pore diameters. To achieve uniform deposition of nanowires, templates were cleaned in the ultrasonic bath for 10 minutes. The electrochemical cell, fabricated in our laboratory using Perspex sheets, was washed in double distilled water. A copper rod of 0.8 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. Prior to the electro-deposition process, a thin film of copper (0.5 μm) was coated onto one side of alumina disc by thermal evaporation technique using Thin Film Coating Unit.

This metal layer along with adhesive copper tape provides a stable substrate (cathode) for the growth of nanowires. Polymer membranes were damaged during thermal evaporation of copper and used as received, or after coating with silver paste manually, for electro-deposition.

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-electrode distance was kept 0.5 cm and a current of 2 mA was applied for 10 minutes using APLAB power supply. Electro-deposition of copper nanowires depends on many factors, namely, inter-electrode spacing, electrolyte composition, temperature and pH value, current density and time of deposition. The influence of current density, temperature and type of electrolyte on the crystallinity of copper nanowires has been reported elsewhere [12]. During our experiments, pH value was adjusted between 4-5, deposition temperature between 30-50^{0}C and we studied the effect of current density on electro-deposition of copper nanowires by varying the current between 2-3 mA.

After the electro-deposition was over, copper foil with template-grown nanowires was kept immersed in 1 M NaOH for 1 hour 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^{0}C for 30 minutes. The cleaned and dried nanowires were mounted on aluminium stubs with the help of double adhesive tape. FESEM (Hitachi S-4300) was used to record cross-sectional and lateral views of grown nanowires at an accelerating voltage of 15 kV using different magnifications. X-ray Diffraction studies were carried out at Sophisticated Analytical

Journal of NanoScience, Nanoengineering & Applications
Volume 1, Issue 1, February, 2011, Pages 1-16.

Instruments Facility (SAIF) set up by Punjab University, Chandigarh using X' Pert PRO (PANanalytical, Netherlands) employing Cu Kα radiation source of $\lambda = 1.5406$ Å.

3. Results and Discussion

3.1 AFM, SEM and FESEM Analysis

Commercial available templates were examined before their use using Atomic Force Microscope (NT-MDT PR 400 Model) installed in our laboratory and Scanning Electron Microscope (Jeol, JSM 6100) facility of Punjab University, Chandigarh. Atomic force microscopic technique [13] shows the two dimensional surface topology of the anodic alumina template with hexagonal pores regularly arranged on the surface (Fig. 1a). The pores appear nearly at the centre of each hexagonal cell. After gold sputtering, using Jeol sputter JFC 1100, SEM micrograph (Fig. 1b) shows the geometrical pattern of pores on the alumina surface of anodisc.

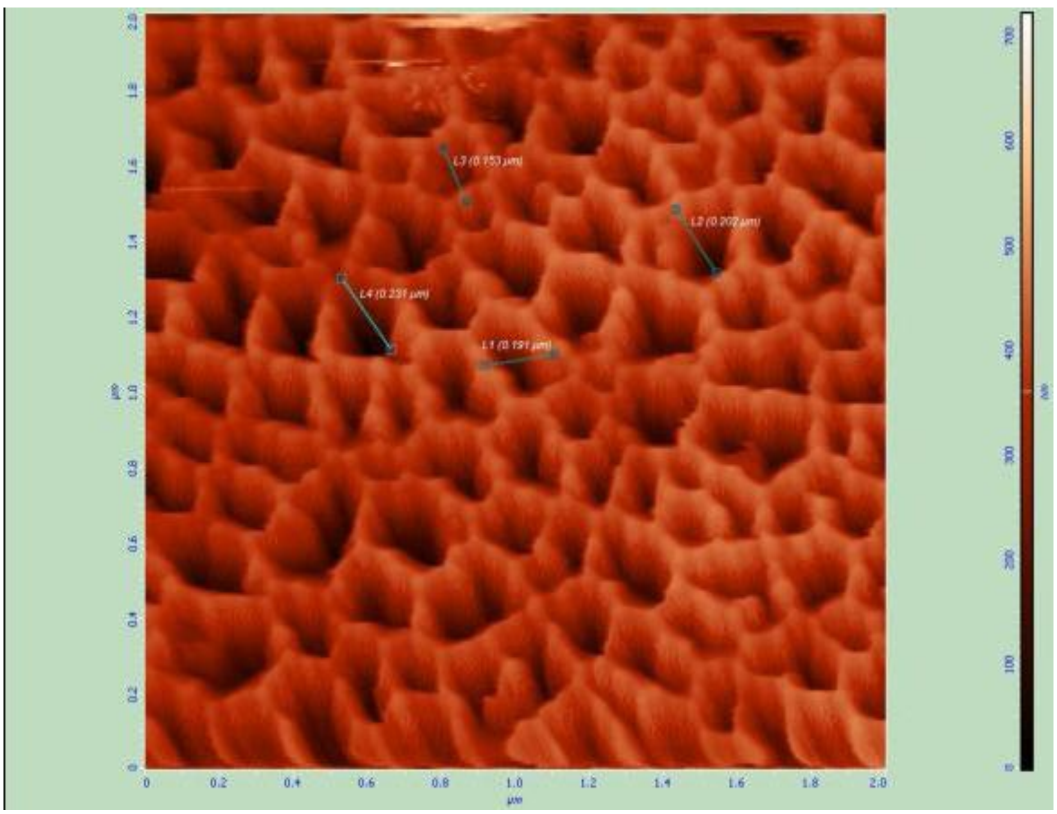


Fig. 1: (a) AFM image of hexagonal pores of anodic alumina template

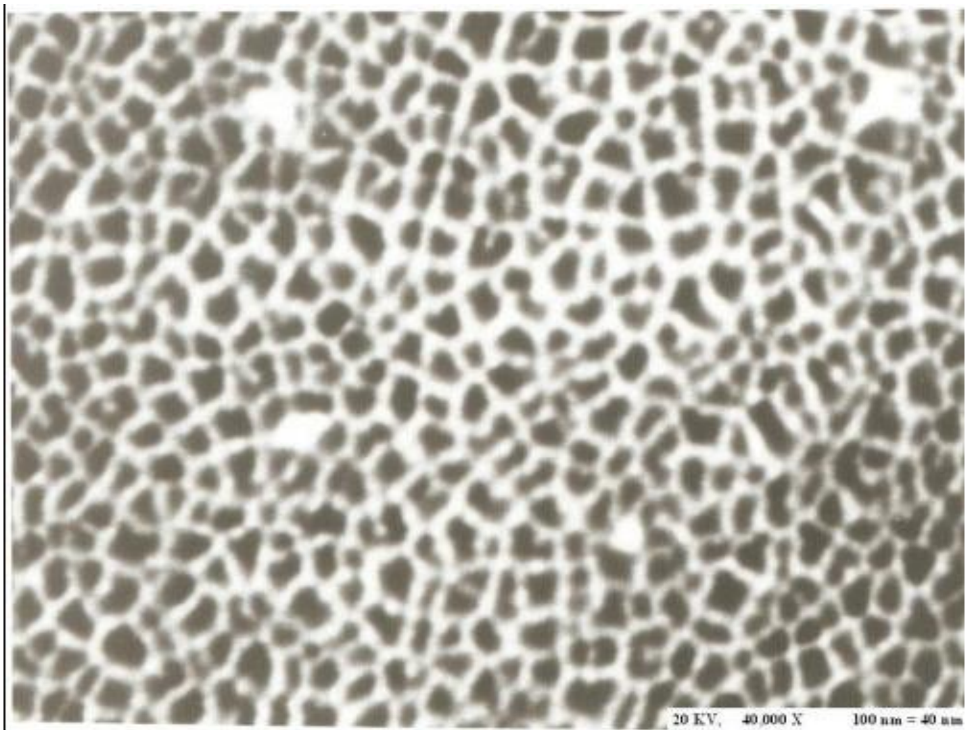


Fig. 1: (b) SEM image of anodic alumina template pores

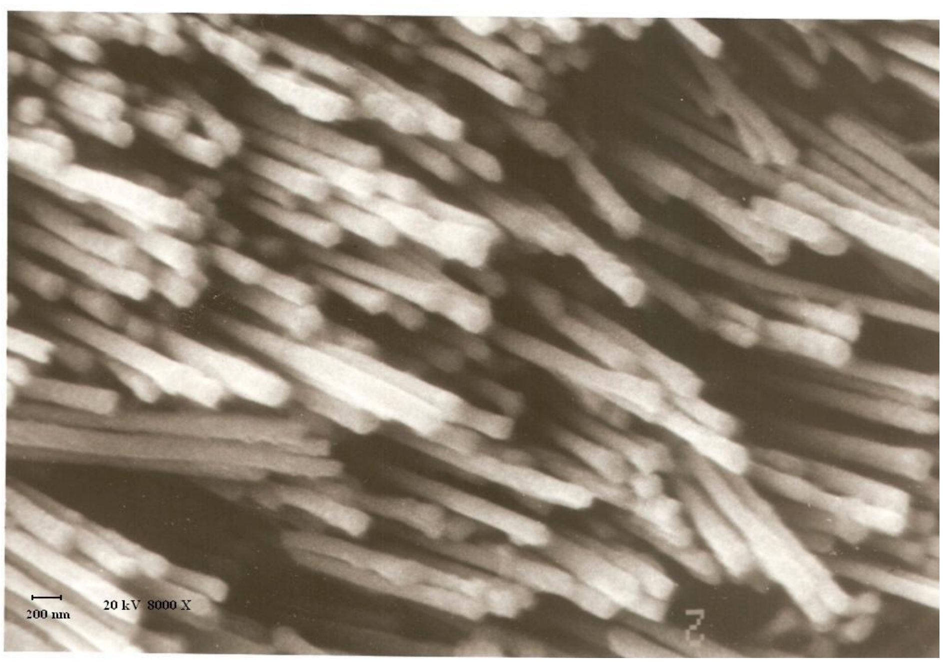


Fig. 2: SEM image of copper nanowires fabricated in anodic alumina template (cross-sectional view, 200 nm dia.)

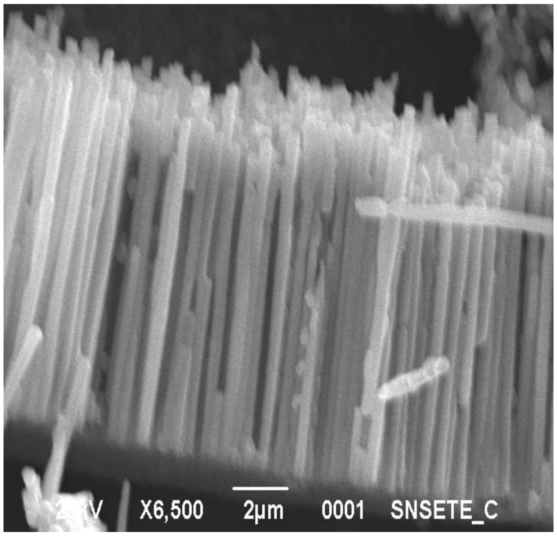


Fig. 3: (a) SEM image of copper nanowires fabricated in AAM under constant current

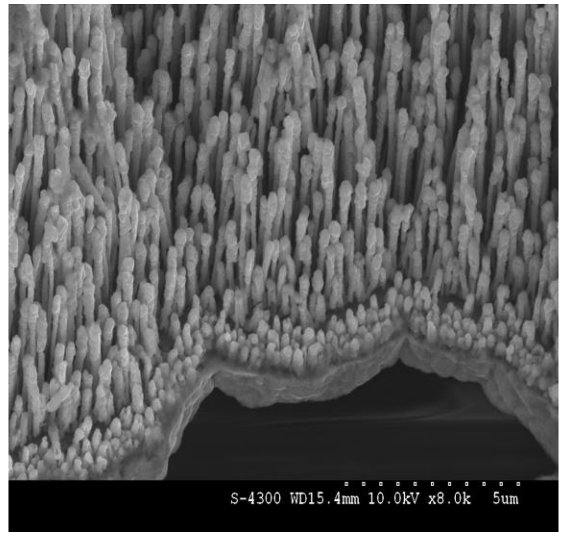


Fig. 3: (b) SEM image of copper nanowires under transient current with capping effect

Copper nanowires liberated from AAM were examined under SEM and FESEM under different magnifications. Two sets of templates were used for growth of copper nanowires. In one set, current density was changed intermittently which resulted in non-uniform growth of nanowires. Figure 2 represents the cross-sectional view of copper nanowires of 200nm diameter grown in alumina template. Figure 3(a) shows the SEM image of copper nanowires array in lateral view, grown under constant current conditions. Figure 3(b) represents the FESEM image of copper nanowires fabricated under transient current conditions, current constantly varied between 2-3 mA. Over-deposition of copper is clearly visible towards the tip of nanowires resulting in capping effect. Nanowires are quite uniform with diameter in the range of 200 nm but they are not perfect cylinders. It has been reported [14] 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.

Electro-deposition of copper nanowires was achieved using polycarbonate membrane with pore diameter of 100 nm as a template and keeping the other conditions identical [11]. Silver paste was coated on the back of polymer template to make it conducting. The polymer template was dissolved in dichloromethane at room temperature. SEM micrograph of grown copper nanowires is shown in Fig. 4. The cross-sectional view of nanowires is somewhat of poor quality and not as smooth as in case of alumina templates.

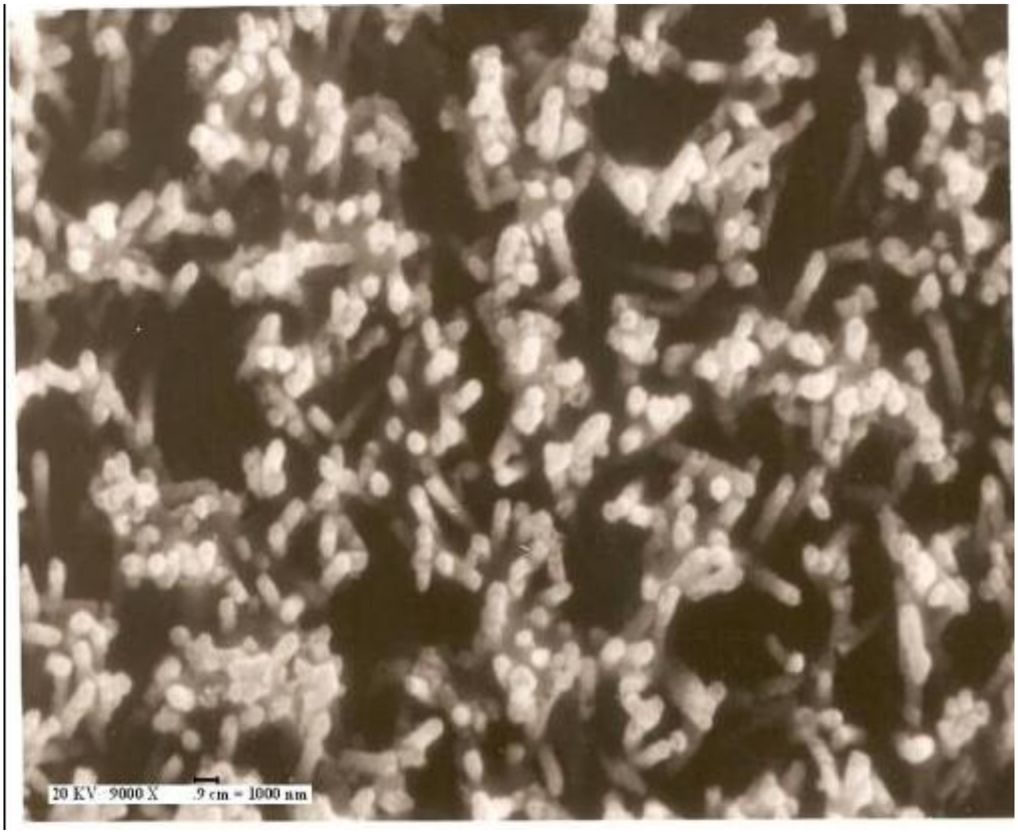
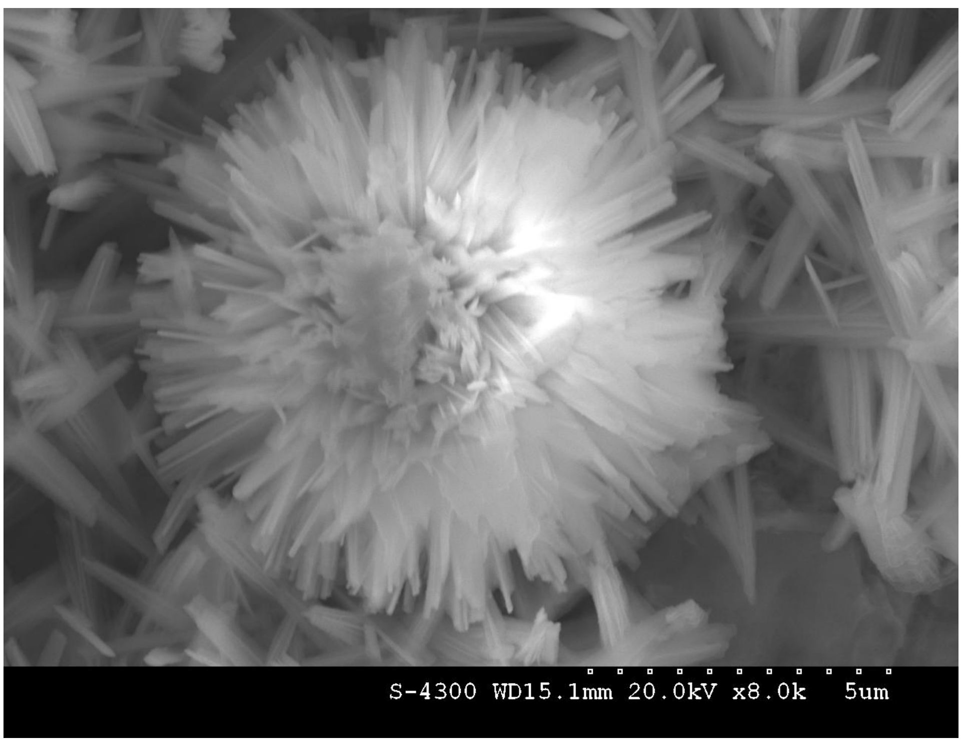


Fig. 4: SEM image of copper nanowires grown in polymer template (cross-sectional view)

We repeated the experiment using polymer templates of 20 nm without using silver paste as a conducting medium. After electro-deposition, the polymer template was dissolved in dichloromethane at room temperature. Instead of nanowires, we observed under FESEM the exotic patterns in the form of microflowers having their petals in nanometer dimension (Fig.5 a,b) and copper buds (Fig. 6 a,b) leading to mushroom effect. Similar results with exotic patterns were reported in our earlier experiment [11]. It is not always possible to get consistent results by repeating experiments using identical conditions of electro-deposition and chance plays a predominant role. It indicates that a law akin to nature's self assembly may be operating in this domain.

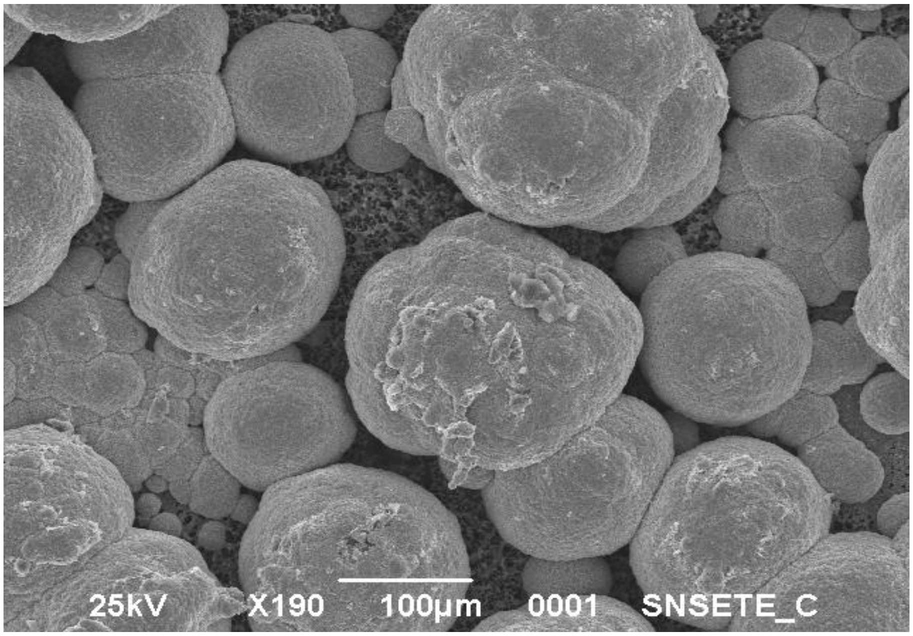
Journal of NanoScience, Nanoengineering & Applications
Volume 1, Issue 1, February, 2011, Pages 1-16.

(a)

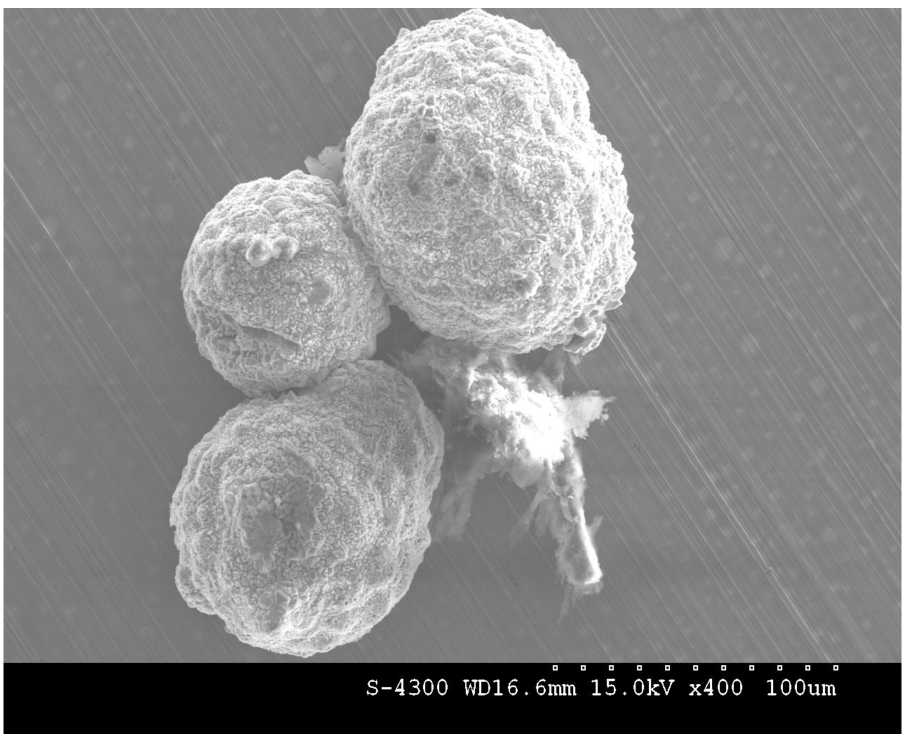


(b)

Fig. 5: (a,b) FESEM micrographs showing flower patterns grown in polymer template



(a)



(b)

Fig. 6: (a,b) FESEM micrographs showing copper buds grown in polymer template

There is as yet no specific theory to explain exotic patterns developed during electro-deposition of copper in anodic alumina or polymer templates. A speculative explanation [15] is provided on the basis of over-deposition. During the growth of copper nanowires in the template pores, the current remains nearly stable until the wires arrive at the template surface. If the electro-deposition process is not stopped at this stage, the current keeps on rising very gradually leading to over-deposition of copper. Flower like morphologies of metal overdeposits have been attributed to the changes in hydrodynamic conditions due to excessive hydrogen evolution during electro-deposition process [16].

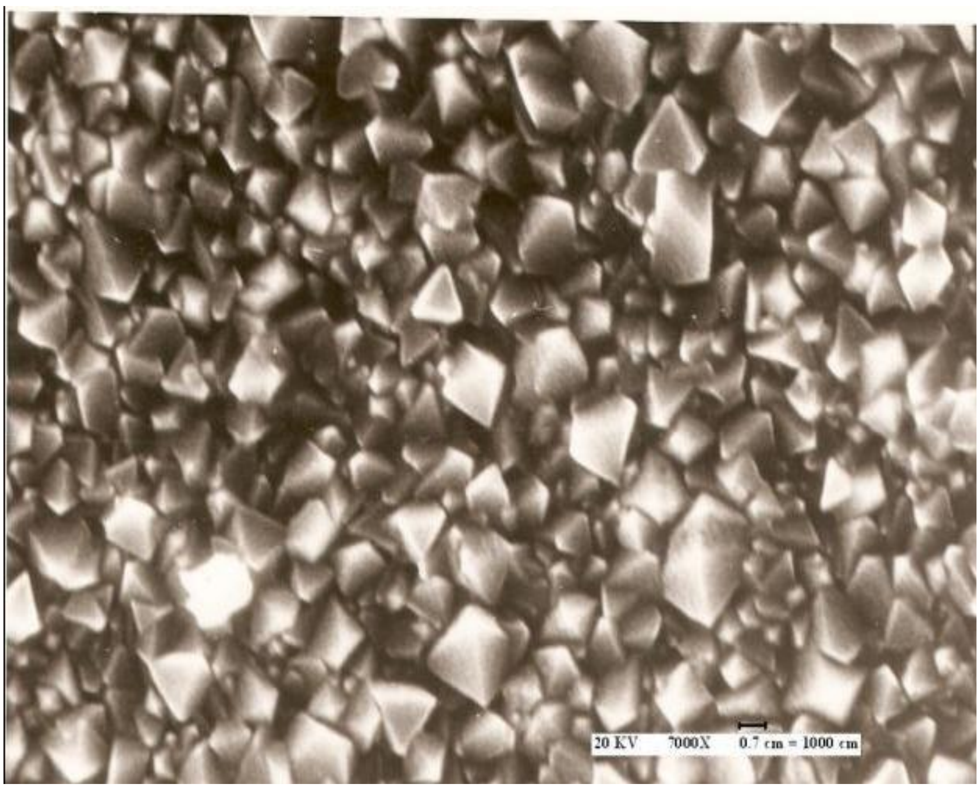


Fig. 7: SEM micrograph of pyramid shaped polycrystalline copper crystals

During our experiments using 20 nm pore diameter polycarbonate template, we had a big surprise in store beyond our imagination! The template was not coated with a conducting layer during electro-deposition. It resulted in failure to grow nanowires but the failure of experiment proved to be a blessing in disguise. Instead of copper nanowires, we observed growth of double pyramid shaped copper crystals (Fig. 7). We could not find any evidence for this phenomenon in published literature on electro-deposition of nanowires.

3.2 X-ray and EDX Analysis

The crystal structure of these pyramid shaped copper crystals has been determined using X-ray diffraction analysis. XRD spectrum (Fig. 8) shows two prominent peaks corresponding to $2\theta = 43.4610$ and 50.5803, with d spacing = 2.082 and 1.804, respectively. These peaks reveal the polycrystalline nature of copper crystals, indicating that preferred growth direction of crystals is the (200) plane. Template based synthesis of single crystal copper nanowires has been reported in literature [12,15,17] with preferred growth direction along (111) plane, but to the best of our knowledge, there is hardly any report for pyramid-shaped polycrystalline copper crystals with a (200) preferred orientation.

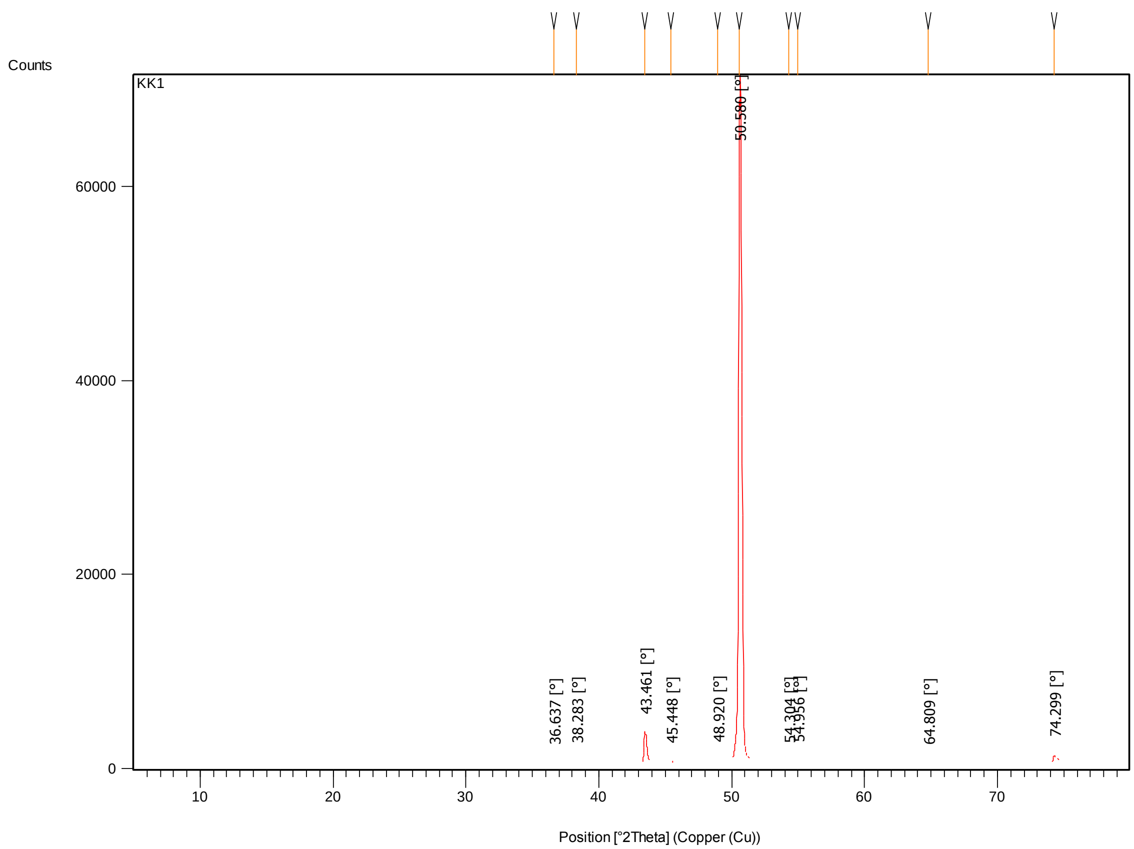


Fig. 8: XRD spectrum of pyramid-shaped polycrystalline copper crystals

The crystallographic structure of copper nanowire arrays was investigated by X-ray diffraction analysis (XRD). For sake of comparison, XRD spectrum of Cu foil used as a substrate was also recorded (Fig. 9). XRD diffractograms were obtained in the 2θ range from 10^0 to 80^0 with a step of 0.02^0, using the Cu Kα radiation source of λ = 1.5406 Å. XRD spectrum (Table 1) shows three prominent peaks corresponding to 2θ = 43.5966, 50.8127 and 74.4331, with d spacing = 2.074, 1.80 and 1.27, and corresponding Miller indices, (111), (200) and (220), respectively. All the peaks can be attributed to the crystalline cubic form of metallic copper [6] and can be indexed to Card ICSD # 064699.

XRD diffractogram (Fig. 10) for copper nanowires was obtained in the 2θ range from 10^0 to 100^0 with a step of 0.02^0, keeping other parameters same as above. There are in all 9 peaks in the spectrum (Table 2), with one insignificant peak at 2θ= 37.3222, which may be due to Cu_2O impurity. Three main peaks are also there as in Fig. 9 but two of them split into double and triple peaks, which may be attributed to X-ray scattering at the substrate. The presence of five prominent diffraction peaks at 2θ angles of 44.1976, 51.3448, 74.8869, 90.6580 and 95.9099 with the most prominent peak at 2θ=44.1976, reveals that the Cu nanowires with face-centered cubic (fcc) crystal structure had been fabricated. These peaks correspond to Cu (111), Cu (200), Cu (220), Cu (311) and Cu (222), respectively, indicating that the preferred growth direction of nanowires is the (111) plane. The strong and sharp peaks indicate that copper nanowires have high degree of crystalline order. All the intense XRD peaks in spectrum (Fig. 10) correspond to and match perfectly with those of polycrystalline Cu standard (Card # ICDD 001-1242). Template based synthesis of single crystal copper nanowires have also been reported in literature [15, 17] with preferred growth direction along (111) plane.

The average size *D* of the crystalline grains in the Cu nanowires is calculated using the Debye Scherrer's formula [18]: $D = 0.9\,\lambda / \beta \cos\theta$, where λ=1.5406 Å is the wavelength of the X-ray radiation used, β is the full width at half maximum (FWHM) of the diffraction peak (0.1338), K, shape factor is assumed to be 0.9 and θ is the Bragg diffraction angle of the most prominent XRD peak. Substituting appropriate values in the formula, the crystallite size value of Cu nanowires comes out to be 1.12 nm. However, the value of crystallite size calculated for Cu foil is of the order of 2.44 nm.

Table 1. XRD spectrum peaks data of copper film

Pos. [°2Th.]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]	Area [cts*°2Th.]
43.5966	0.0612	2.07438	100.00	847.65
50.8127	0.0816	1.79542	48.53	548.43
74.4331	0.1428	1.27358	11.94	236.07

Table 2. XRD spectrum peaks data of copper nanowires

Pos. [°2Th.]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]	Area [cts*°2Th.]
37.3222	0.4015	2.40741	1.81	32.89
44.0674	0.1224	2.05330	73.55	550.50
44.1976	0.1338	2.04755	100.00	605.43
50.7219	0.1338	1.79842	9.18	55.58
51.0435	0.0612	1.78784	16.51	61.77
51.3448	0.0816	1.77806	75.85	378.50
74.8869	0.2448	1.26698	7.01	104.91
90.6580	0.2040	1.08317	10.76	134.23
95.9099	0.1428	1.03727	6.50	56.79

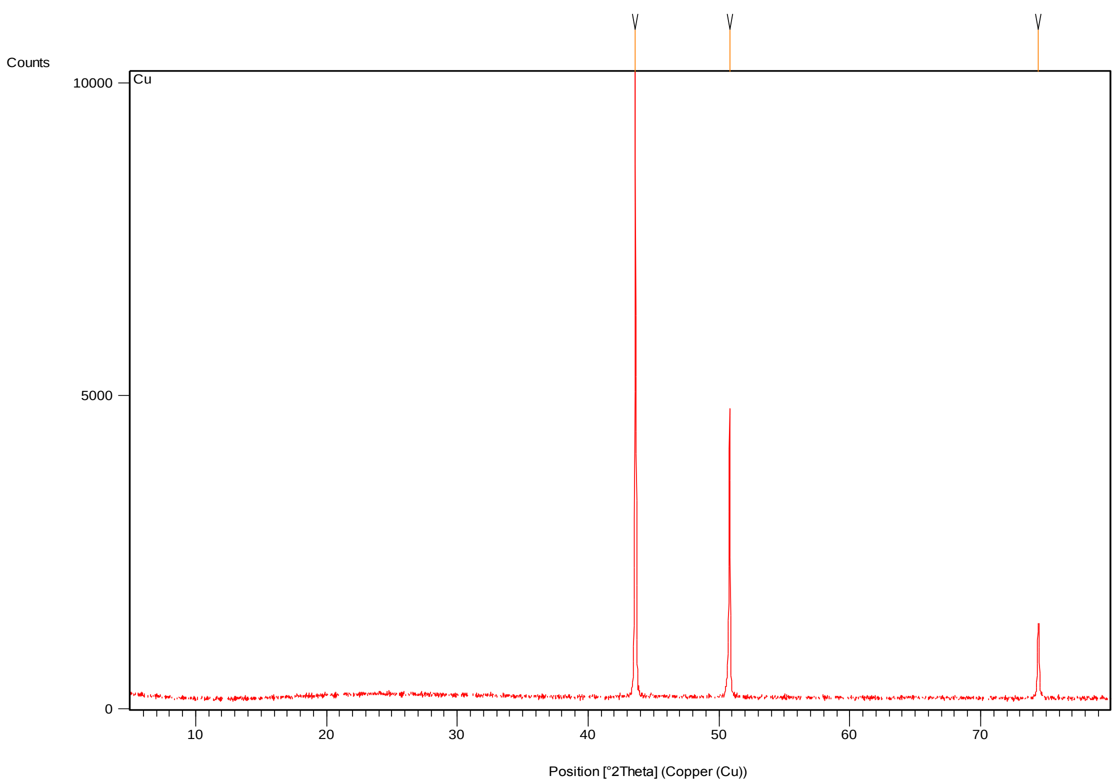


Fig. 9: XRD spectrum of Copper film serving as a substrate

Journal of NanoScience, Nanoengineering & Applications
Volume 1, Issue 1, February, 2011, Pages 1-16.

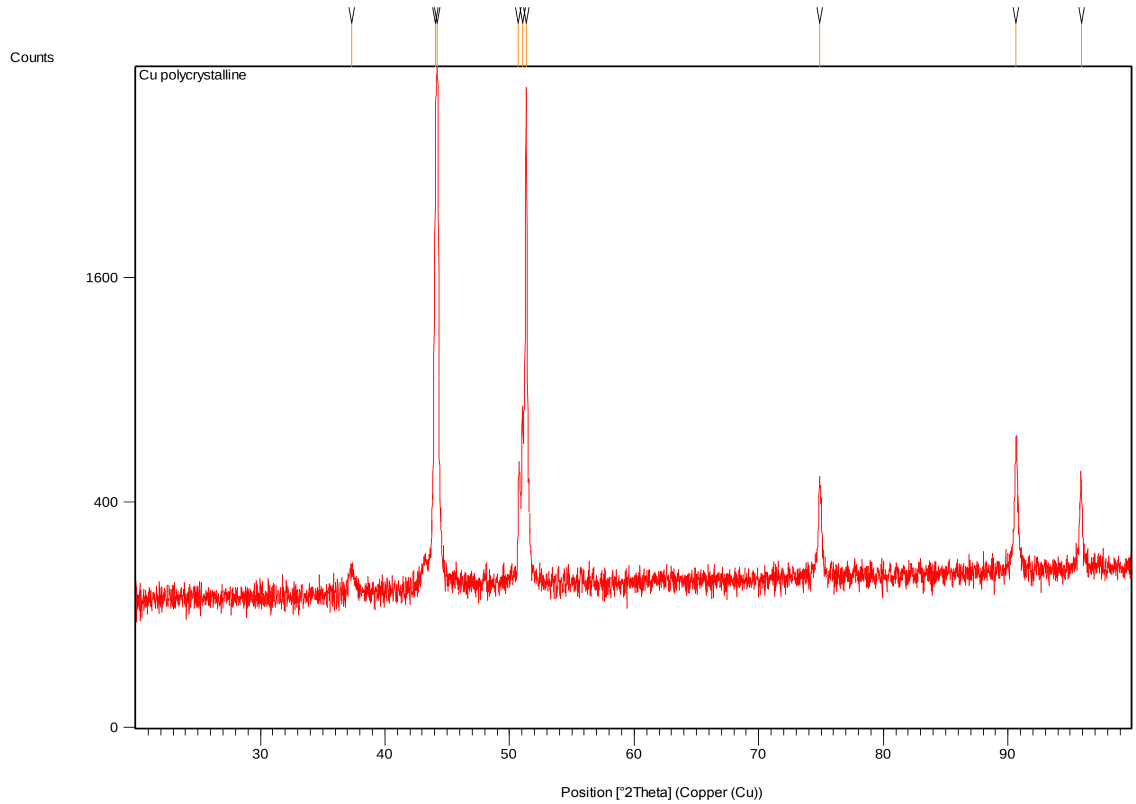
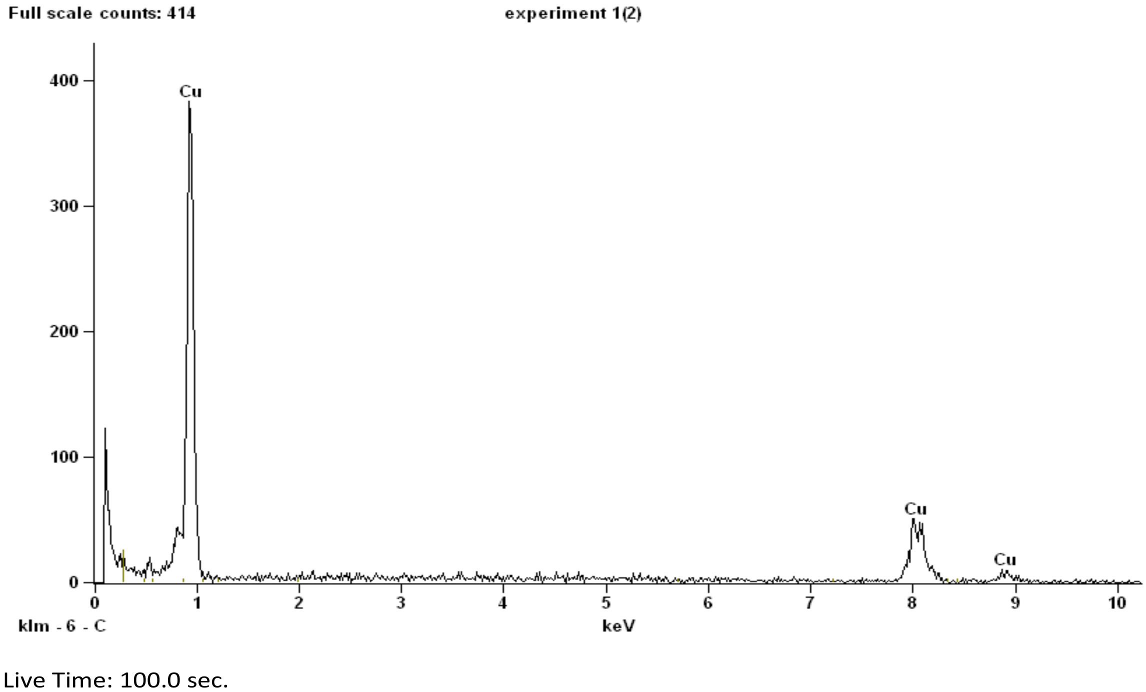


Fig. 10: XRD spectrum of Copper nanowires of 200 nm diameter

Energy dispersive X-ray spectroscopic (EDX) analysis of Cu nanowires was carried out at FESEM facility of CSIO, Chandigarh to determine chemical composition of nanowires. The spectrum (Fig. 11) reveals 3 peaks of copper with 100% pure copper content and no traces of any impurity in Cu nanowires. It also establishes that multiple XRD peaks are not due to any impurity but due to polycrystalline nature of Cu nanowires. Gao et al. [19] observed that when Cu^{2+} ions are deposited on to the cathode surface, a certain amount of over-potential is needed for the nucleation and growth of nanowires. The higher the over-potential, the higher the nucleation rates, which will make the deposited Cu nanowires have a polycrystalline nature. It could be deduced that every Cu nanowire in the array has the same crystalline structure.



Quantitative Results for: experiment 1(2)

Element Line	Weight %	Weight % Error	Atom %	Atom % Error
Cu K	100.00	+/- 7.49	100.00	+/- 7.49
Total	100.00		100.00	

Fig. 11: EDX spectrum and elemental composition of Copper nanowires

4. Conclusions

Our investigations confirm that electro-deposition of copper nanowires in anodic alumina is the simplest route to nanotechnology. The copper nanowires reveal effect of high current density resulting in over-deposition in the form of capped growth, and not as perfect cylinders. The aspect ratio is very high, of the order of 300. XRD analysis shows fcc crystalline nature of nanowires with preferred growth direction in the (111) plane. The crystallite size of nanocrystals in copper nanowires is determined to be 1.12 nm. Over-deposition results in growth of copper buds and beautiful flower patterns. Pyramid-shaped polycrystalline copper crystals are observed for the first time during failure to fabricate copper nanowires using electro-deposition technique. Due to high aspect ratio, copper nanowires may be used as field emitters [20]. Possible applications of nanoflowers as optoelectronics devices or sensors, in catalysis, and solar cells will be of definite interest in future studies [21].

Acknowledgements

The authors are thankful to the Principal, DAV Institute of Engineering & Technology, Jalandhar and DAV College Managing Committee, New Delhi for providing research grant to set up Research Centre and Nanotechnology Laboratory in Jalandhar. FESEM analysis was carried out at CSIO, Chandigarh. Authors wish to record their appreciation to Dr Pawan Kapur, Director CSIO and Dr Lalit M. Bharadwaj, Head Nanotechnology Group at CSIO for providing research facilities. Dr Inderpreet Kaur and her research team also deserve my appreciation for rendering all possible help during characterization. Mohinder Singh and Jagtar Singh at SAIF, PU Chandigarh provided all help in SEM and XRD analysis of samples, respectively, whenever I approached them.

References

1. Sarkar J. et al. *Bulletin Material Science* 2007. 30 (3). 271-290p.
2. Agarwal R. and Lieber C. M. *Applied Physics A* 2006. 85. 209-215p.
3. Liu Chuan-Pu et al. *Recent Patents on Nanotechnology* 2007. 1. 11-20p.
4. Cao D. and Liu D. *Advances in Colloid and Interface Science* 2008. 136. 45-64p.
5. Sun Shin H. et al. *Materials Letters* 2009. 63. 397- 399p.
6. Ingunta R. et al. *Electrochemical Commununication* 2008. 10. 506-509p.
7. Fang C. et al. *Journal Electrochemical Society* 2007. 154. D45- D49p.
8. Motoyama M. et al. *Journal Electroanalytical Chemistry* 2005. 584. 84p.
9. Rathmell A. R. et al. *Advanced Materials* 2010. 22. 3558-3563p.
10. Lai M. and Riley D. J. *Journal Colloid & Interface Science* 2008. 323. 203-212p.
11. Virk H. S. et al. *Journal Nano Research* 2010. 10. 63- 67p.
12. Toimil Molares M. E. et al. *Advanced Materials* 2001. 13. 62-65p.
13. Menon L. *Quantum Dots and Nanowires.* Hari Singh Nalwa and S. Bandhopadhaya (Eds.). American Scientific Publishers. USA. 2003. 142-187 p.
14. Schonenberger C. et al. *Journal Physical Chemistry B* 1997. 101. 5497- 5505 p.
15. Gao T. et al. *Journal Physics: Condensed Matter* 2002. 14. 355-363p.
16. Kumar S. et al. *Superlattices and Microstructures* 2008. 43. 324-329p.
17. Mingliang. T. et al. *Nano Letters.* 2003. 3. 919-923p.
18. Cullity D. B. Massachusetts. USA. *Elements of X-ray Diffraction.* Addison-Wesley. 1956.
19. Gao T. et al. *Applied Physics A: Materials Science & Processing* 2001. 73. 251-254p.
20. Brotz J. et al. *Microstructure Analysis in Material Science* Freiberg, June 15-17. 2005.
21. Kharisov B. I. *Recent Patents on Nanotechnology* 2008. 2. 190-200p.