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Fabrication of polycrystalline copper nanowires by electrodeposition in anodic alumina membrane and their characterization

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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 diameter 200 nm using anodic alumina membranes (AAM) as templates. Template-based growth of copper nanowires has been realized using conventional electrodeposition technique in an electrochemical cell designed in our laboratory. FESEM micrographs and EDX reveal morphology and chemical composition of fabricated nanowires. The morphology of nanowires shows some interesting features. XRD spectrum reveals polycrystalline nature of Cu nanowires with crystallite size of 1.222 nm. I-V characteristics of nanowires using dual source meter (Keithley Model 4200 SCS) are investigated for the purpose of device making.

Keywords: Cu nanowires, Electrodeposition, Template synthesis, Anodic alumina membrane, I-V characteristics.

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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. 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 (1-3).

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. 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 (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 membranes of 200 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 (9):

(i) It is performed under mild conditions rather than requiring high temperatures, high vacuum or expensive instrumentation; (ii) templated electrodeposition has a relatively high growth rate; (iii) the morphology of deposited materials depends on the shape of template pores; (iv) the dimensions of the materials obtained can be tuned by tuning of the template pore size; (v) two or more components can be easily deposited into the membrane sequentially to form multi-segmented materials or hetero-junctions.

2. Materials and Methods

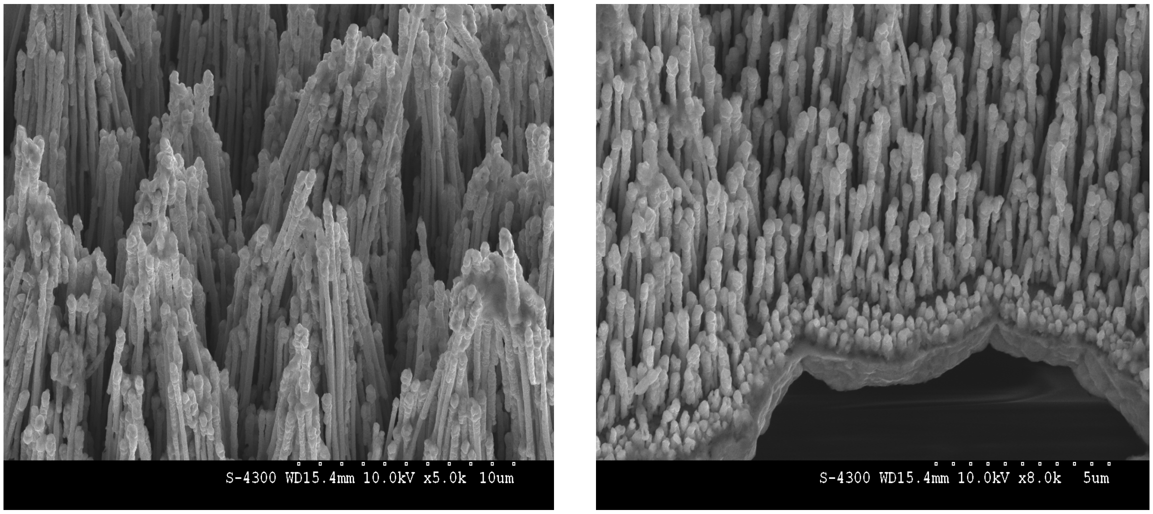
The electrodeposition technique used in our experiment (10) is similar in principle to that used for the electroplating process. Commercial anodic alumina membranes (Anodisc 25 made by Whatman) having an average pore diameter of 200 nm, a nominal thickness of 60 μm and a pore density of 10^9 pores/ cm^2, were used as templates. 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 sputtered onto one side of alumina disc. This metal layer along with adhesive copper tape provides a stable substrate for the growth of nanowires.

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 using APLAB power supply. Electrodeposition 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 (11). We studied the effect of current density on electrodeposition of copper nanowires in our experiment.

After the electrodeposition was over, copper foil with template-grown nanowires (AAM) was divided into two parts. One part was kept for study of I-V characteristics in-situ using Dual Source Meter (Keithley Model 4200 SCS) with platinum probes for contacts. The other part 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 50^0C for 30 minutes. The cleaned and dried nanowires were mounted on aluminium stubs with the help of double adhesive tape. Field Emission Scanning Electron Microscope (FESEM, Hitachi S-4300) was used to record cross-sectional and lateral views of grown nanowires at an accelerating voltage of 15kV using different magnifications. X-ray Diffraction studies were carried out at Sophisticated Analytical Instruments Facility (SAIF) set up by Punjab University, Chandigarh using X' Pert PRO (PANanalytical, Netherlands) using Cu Kα radiation.

3. Results and Discussion

Copper nanowires liberated from AAM were examined under 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. Fig. 1 (a,b) represents the cross-sectional and lateral views of copper nanowires grown in alumina template. Overdeposition of copper is clearly visible towards the tip of nanowires. Nanowires are quite uniform with diameter in the range of 200 nm but they are not perfect cylinders. It has been reported (12) 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. For sake of comparison, Fig. 2 represents copper nanowire arrays grown under constant current density with uniform diameter and devoid of any overdeposition effect. The gaps between nanowire arrays are caused by strain created during dissolution of anodic alumina template or due to un-intentional shaking.



(a) (b)

Fig. 1(a,b) FESEM images of Copper nanowires (cross-sectional & lateral views)

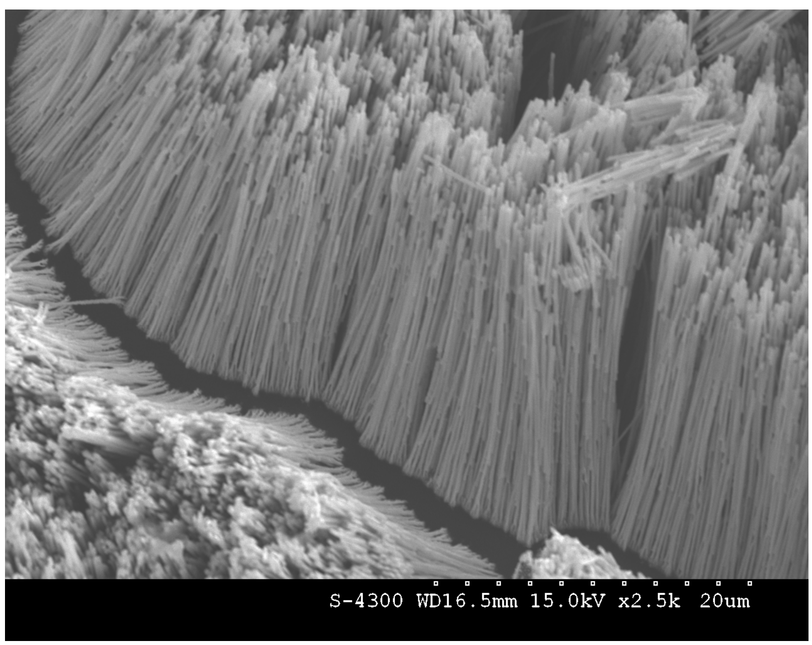


Fig. 2. FESEM image of copper nanowires grown under constant current density

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. 3). XRD diffractograms were obtained in the 2θ range from 10^0 to 80^0 for Cu film and 20^0 to 100^0 for Cu nanowires, with a step of 0.02^0, using the Cu Kα radiation source of λ = 1.5406 Å. XRD spectrum (Fig. 3) 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 peaks can be attributed to the crystalline cubic form of metallic copper (13). XRD spectrum of copper nanowires (Fig. 4) shows some interesting results. There are in all 9 peaks in the spectrum; with one additional peak at 2θ= 37.3222, which may be due to Cu_2O impurity. Three main peaks are also there as in Fig. 3 but two of them split into double and triple peaks, which may be attributed to X-ray scattering at the substrate. The polycrystalline nature of copper nanowires is revealed by the presence of five 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. 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. Template based synthesis of single crystal copper nanowires have also been reported in literature (14-15) with preferred growth direction along (111) plane.

The polycrystalline structure of copper nanowires has been attributed to fabrication conditions. Gao et al. (14) consider that higher overpotentials used during electrodeposition result in polycrystaline character of nanowires. Toimil Molares et al. (11) proposed that temperature influences the crystallinity of copper nanowires; at room temperature they observed polycrystalline nature which disappeared at 60 ^{0}C.

The average size *D* of the crystalline grains in the Cu nanowires is calculated using the Debye Scherrer's formula (16): $D = 0.9\ \lambda / \beta \cos\theta$, 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 almost double, of the order of 2.44 nm.

Energy dispersive X-ray spectroscopic (EDS) analysis of Cu nanowires was carried out at CSIO, Chandigarh to determine chemical composition of nanowires. The spectrum (Fig.5) 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.

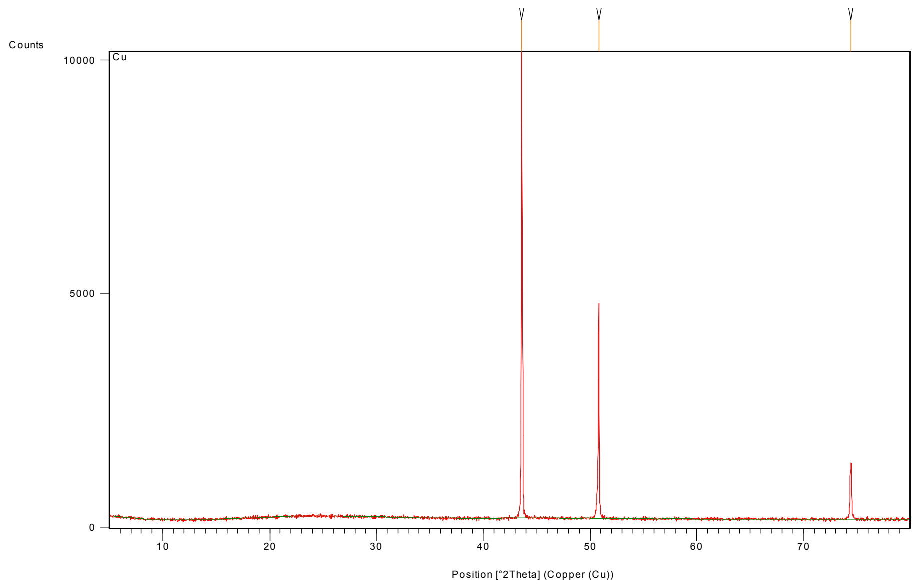


Fig. 3. XRD spectrum of Copper film serving as a substrate

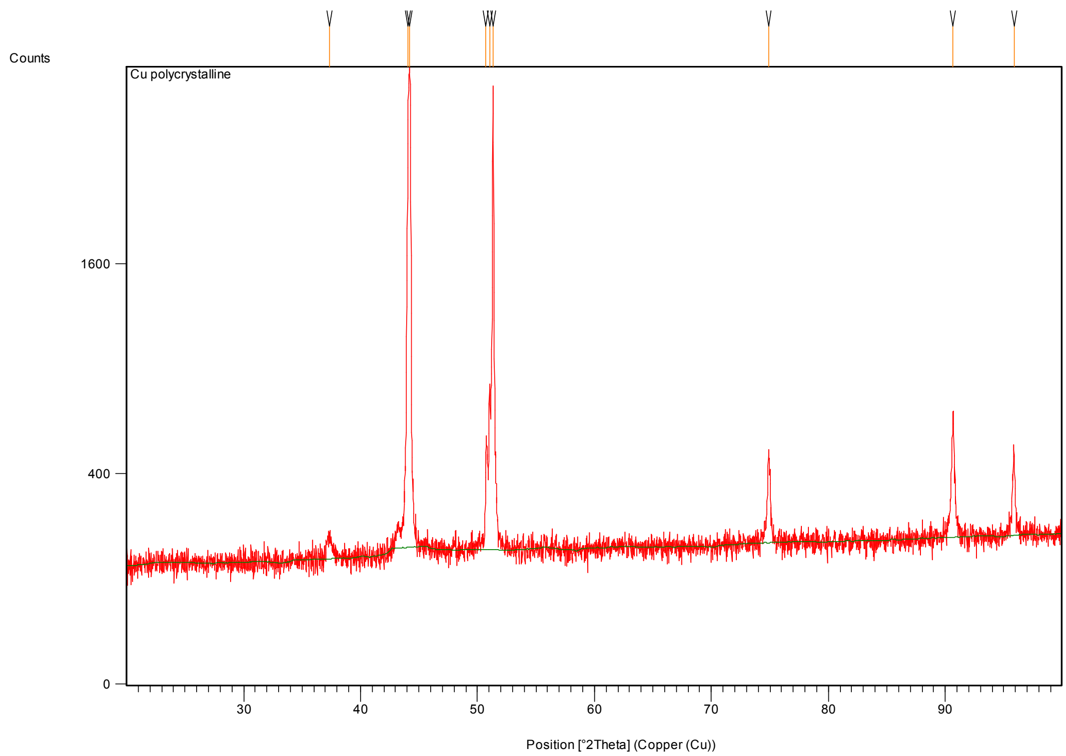
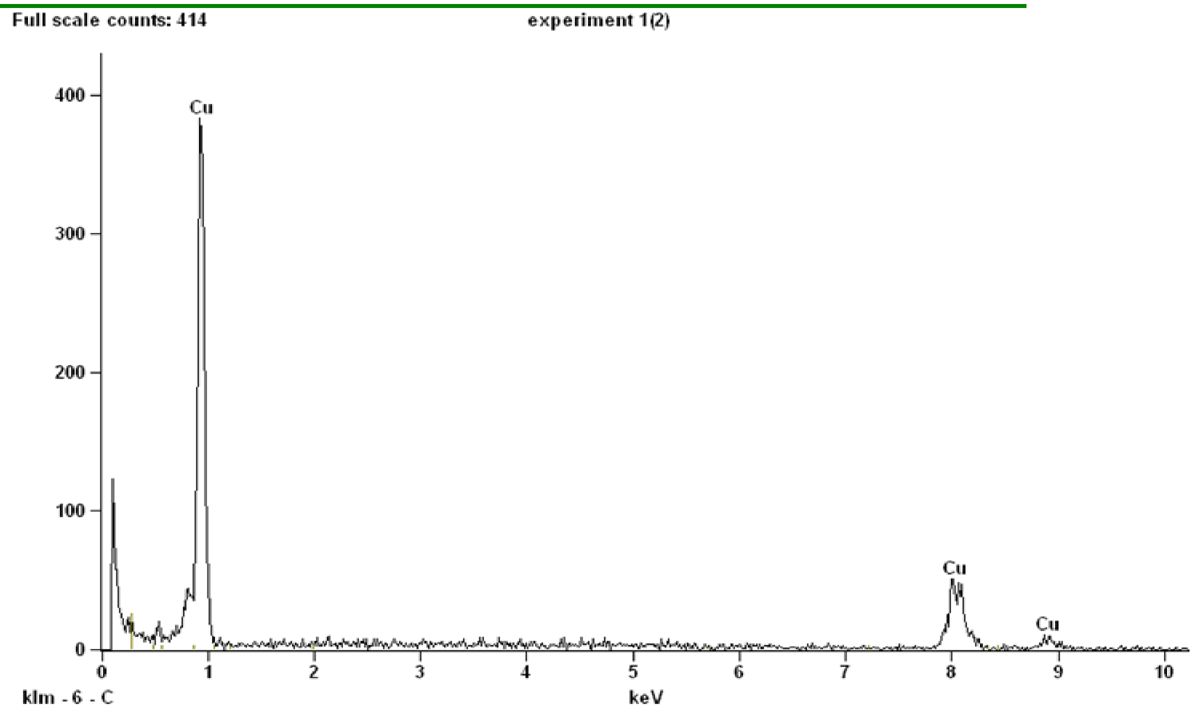


Fig. 4. XRD spectrum of Copper nanowires of 200 nm diameter

Table 1. XRD peaks data for polycrystalline 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



Live Time: 100.0 sec.

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. 5. EDS spectrum and elemental composition of Copper nanowires

I-V characteristics of copper nanowires were recorded in-situ as grown in pores of anodic alumina membrane (AAM). The combination of copper nanowires on alumina, an insulator, results in the formation of a strange device. I-V plot (Fig. 6) shows some interesting features of resonating tunneling diode in the forward bias mode but nothing special in the reverse bias mode. The offset in I-V plot around zero voltage may be due to slight non-ohmic characteristic of the contact, or due to quantum confinement behaviour of electrons traversing through copper nanowires.

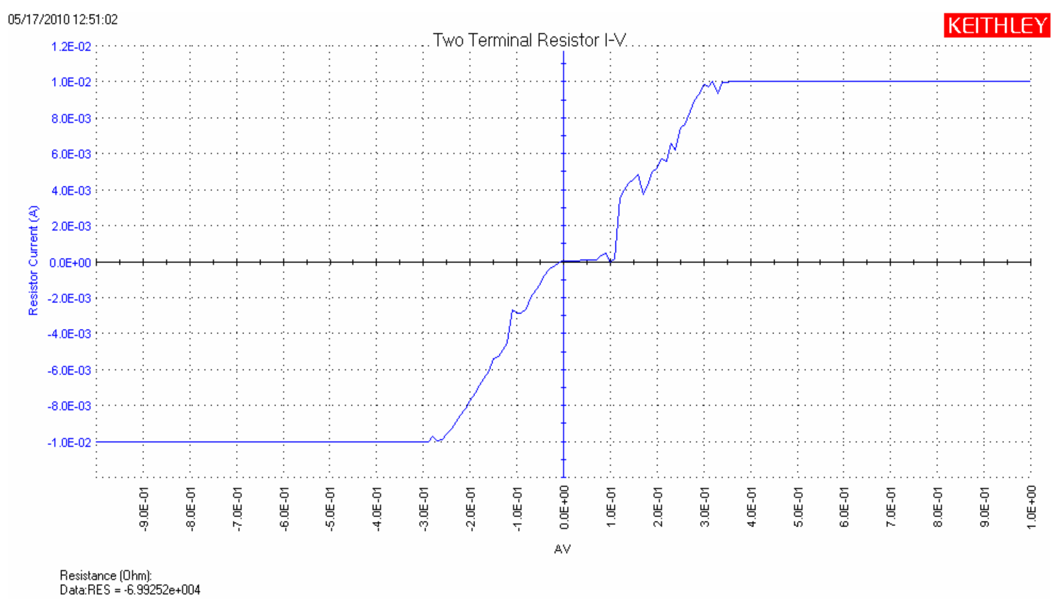


Fig. 6. I-V characteristics of copper nanowires grown in-situ in AAM

4. Conclusions

Our investigations confirm that electrodeposition of copper nanowires in anodic alumina is the simplest route to nanotechnology. The copper nanowires reveal effect of high current density resulting in overdeposition 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 polycrystalline nature of nanowires with preferred growth direction in the (111) plane. The crystallite size of nanocrystals in copper nanowires is 1.12 nm. EDS spectrum confirms 100% pure copper content of nanowires. I-V characteristics do not conform to normal p-n junction behaviour and need further investigation. Due to high aspect ratio, copper nanowires may be used as field emitters.

Acknowledgement

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