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SYNTHESIS AND CHARACTERIZATION OF COPPER NANOWIRES USING NUCLEOPORE POLYCARBONATE MEMBRANES

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ABSTRACT

In this paper, copper nanowires have been successfully grown into the pores of polycarbonate membranes through potentiostatic electrodeposition. The morphology and structural property of the copper nanowires have been investigated by using field emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD) technique. I-V characteristic has been observed by using KEITHLEY source meter and it behaves like ohmic. The optical property of the wires has been studied by using UV-visible spectroscopy. Thereafter Field emission properties were studied using Fowler and Nordheim theory.

Keywords: - Track Etch Membranes, Electrodeposition, Copper Nanowires, FE-SEM, XRD, I-V characteristics, Field emission

1. INTRODUCTION

Research on nanomaterials is continuously increasing due to their wide range of applications in the field of electronics [1], magnetism [2-4] and optics [5-7]. Among the different methods available for the fabrication of metallic nanowires, template method is the most suitable method used for the creation of very thin wires with high aspect ratio as high as 1000. The track etch method involves the irradiation of the polymer film by swift heavy ion produces a damage tracks along the ion trajectory [8-9] .These tracks are then chemically etched into a particular solution and are converted into pores. By varying the ion fluence and the etching conditions, pores of different sizes and geometries are possible. This template technique enables the fabrication of wires with various shapes, in particular, conical or cylindrical. As template, track etched membranes (polycarbonate membranes of pore diameter 100 nm) commercially available of Whatmann, UK have been used in this paper. Compared to the other different techniques like electroless method, sol-gel template synthesis, chemical vapour deposition, polymerization reaction etc., electrodeposition method is a very simple and useful method [10-12]. The most important advantage of this technique is that growth rate can be easily controlled and it produces high quality nanowires with a very smooth surface.

2. EXPERIMENTAL DETAILS

In the present work, nucleopore polycarbonate membranes (Whatmann, UK) of pore size 100 nm and thickness 10 um have been used as templates for the fabrication of copper nanowires using electrodeposition technique. For the purpose of deposition, a specially designed two electrode electrochemical cell has been used as described by Raminder et al. [13]. A single sided conductive adhesive copper tape (3M) is fixed on the cathode of the electrochemical cell. Then a polycarbonate membrane has been placed on above this cathode. A limited portion of the membrane placed on top of the substrate was selected for electrodeposition by using O-ring. For electrodeposition of copper into the pores of polycarbonate membranes, an electrolyte consisting of $CuSO_4$.5 H_2O and (10-11 drops) of H_2SO_4 has been used. The potenstiostatic electrodeposition has been carried out for 6 minutes at 0.6 V and the current varies from 0.013 A to 0.012 A at room temperature (30ºC). When the deposition is approximately completed, immediately remove the electrolyte solution from the cell and then washed the sample with double distilled water and finally dried in air to reveal the deposited material within the template for further characterization. Then these nanostructures are retrieved on substrate by dissolving the polycarbonate membranes in dichloromethane (CH_2Cl_2). The morphology of the as-synthesized copper nanowires have been studied by MIRA//TESCAN field emission Scanning Electron Microscopy (FE-SEM). The structural properties of the copper nanowires have been determined by using XRD-7000 SHIMADZU. The optical properties of the nanowires have been studied using UV-visible 1800 Spectrophotometer. I-V characteristic has been observed using KEITHLEY 2400 source meter.

3. RESULTS AND DISCUSSION

3.1 Growth of copper nanowires array

To understand the electrodeposition process, we have done the (I-t) curve experiments. Four different regions are formed during the deposition process. In the first region, the sharp increase in current indicates the formation of charge of double layer. Second region shows the decrease of current due to the creation of diffusion layer. After that, when the current remains constant, it shows that the wires reaches the upper surface. In the fourth region, caps are formed with the increase of current.Fig.1 shows the graph between current and time during the electrodeposition of copper into polycarbonate membranes.

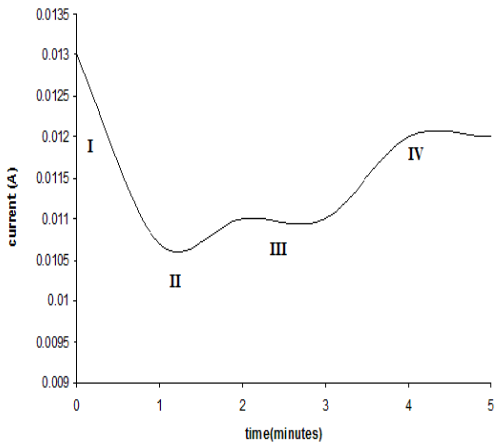

Figure 1: Variation of current with time during potentiostatic electrodeposition of copper into the pore diameter of 100 nm polycarbonate membranes.

3.2 SEM characterization

The morphology of the copper nanowire arrays have been investigated by using field emission scanning electron microscopy (FE-SEM). For morphological study, first the rinsed and dried samples in which the polycarbonate membrane have been dissolved were placed on specially designed aluminum stub with the help of double sided carbon tape and then coated with a layer of carbon in Quoram 150 Sputter Coater System and after that it is viewed under field emission scanning electron microscope at an accelerating voltage of 15 KV. Fig.2 shows the SEM image of copper nanowires of pore diameter 100 nm.

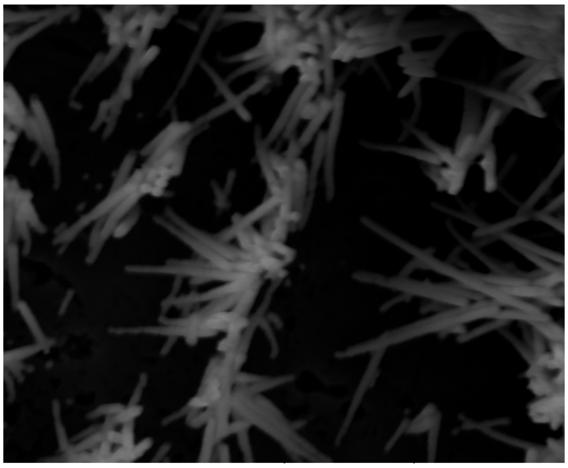

Figure 2: SEM image of the copper nanowires of pore diameter 100 nm.

3.3 XRD characterization

X-ray diffraction has been employed to determine the crystal structure and orientation of the fabricated copper nanowires. X-ray diffraction has been carried out using XRD-7000 Shimadzu. The target used is copper and its characteristic wavelength is (λ=1.54056 Å).X-ray diffraction of the fabricated copper nanowires into the pores of polycarbonate membranes are shown in fig.3. Three peaks are observed in the span ranging 2θ from 10º to 80º at 43.31, 50.46 and 74.21 that corresponds to (111), (200) and (220) planes, respectively. These lattice planes indicates that face centered cubic structure (fcc) of the copper nanowires have been fabricated and it is confirmed by using selection rules or extinction rules as shown in table 1.

The strongest preferred crystallographic direction in XRD spectrum has been determined by using texture analysis. Harris formula [14] has been used to find out the textured coefficient of the preferred orientation and it is represented as:

$$TC(hkl) = \frac{\frac{I(hkl)}{I_0(hkl)}}{N^{-1}\Sigma \frac{I(hkl)}{I_0(hkl)}}$$

Where TC (hkl) is the textured coefficient of (hkl) plane, I (hkl) is the calculated intensity of (hkl) plane, I_0 (hkl) is the standard intensity of the corresponding plane given in JCPDS data [15] and N is the reflection number. The analysis showing a strong texturing (Refer Table 2) along (200) planes. Table.2 shows the calculated values for the intensity of synthesized copper nanowires.

Table 1: Determination of Lattice structure

2θ	Sinθ	$Sin^2θ$	Ratios	Normalized ratios	Lattice planes
43.36	0.3694	0.1364	1.00	3.00	(111)
50.44	0.4261	0.1815	1.33	3.99≈4	(200)
74.21	0.6033	0.3639	2.66	7.98≈8	(220)

Table 2: Determination of Texture coefficient

d values (Å) Standard	d values (Å) Calculated	Lattice planes (hkl)	Intensity Standard (I_0)	Intensity Calculated(I)	Texture coefficient P (hkl)
2.088	2.08	(111)	100	19.57	0.2307
1.808	1.791	(200)	49	100	2.4063
1.278	1.283	(220)	28	8.62	0.3629

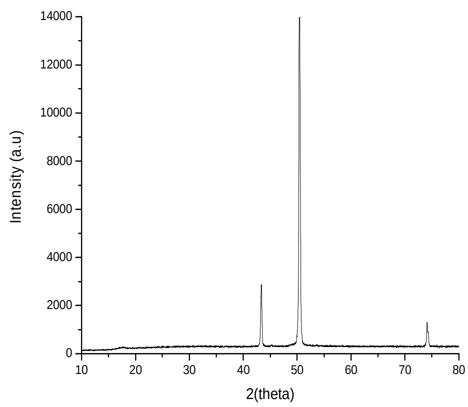

Figure 3: X-Ray diffraction spectrum of the copper nanowires of pore diameter 100 nm.

3.4 UV-visible studies

The optical properties of copper nanowires such as absorption edge and energy band gap have been investigated by using UV-visible 1800 spectrophotometer. The optical absorption spectra of copper nanowires are shown in fig.4. It is clearly shown from the absorption spectra that the optical absorption edge moves towards the visible region (i.e. shorter wavelength). From the graph between the absorption coefficient and wavelength, the optical band gap is determined by using the Tauc relation [16] given as:

$$(\alpha h\nu)^n = B\,(h\nu - E_g)$$

where 'n' is an index and can take different values i.e. 2, 3, 1/2 and 1/3 depending on mechanism of inter band transitions, α is the absorption coefficient ,B is constant called band tailing parameter, hν is the incident photon energy and E_g is the optical band gap energy. The value n=1/2 gives the best linear fit for the Tauc relation that corresponds to the indirect transitions. By extrapolating the linear portion of this plot, we can calculate the band gap energy. The optical band gap energy of the fabricated copper nanowires is calculated to be 2.6 eV.

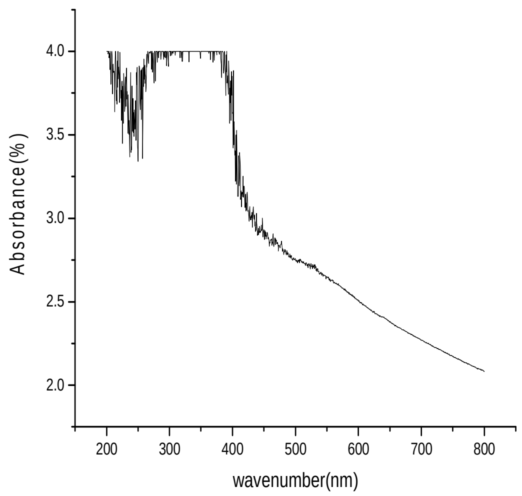

Figure 4: UV-Vis Absorption curve of the copper nanowires of pore diameter 100 nm.

3.5 I-V characterization

The *in- situ* I-V characteristics of nano structures was carried out at room temperature by leaving the structures embedded in the insulating template membrane itself. A KEITHLEY 2400 source meter was used for the measurement. Fig.5 shows the voltage vs current characteristics for the copper nanowires, it's the collective behavior of nanowires lying parallel to each other. The trace shows that nano structures behave like ohmic, indicating metallic behavior with a resistance of 11.82E-6 Ω at room temperature.

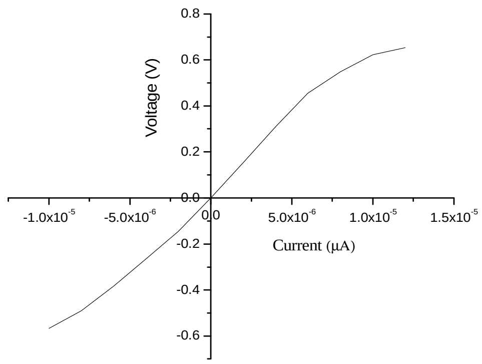

Figure 5: Variation of current with voltage for ectrochemically grown copper nanowires.

3.6 Field Emission Studies

The tips of the synthesized arrays, which had their axes perpendicular to the substrate, were used to act as emitters. Bottom end (semiconducting substrate) was stuck on a copper substrate with the help of silver paste and was used as cathode, experimental setup shown in fig.6. Field emission experiments were carried out at room temperature 29 ºC and at a pressure of 5×10^{-3} Torr. Generally, field emission is characterized using the theory of Fowler and Nordheim [17-26], which predicts a linear relationship between $\ln(I/V^2)$ and V^{-1}. According to the modified FN theory, the current density J from the tip-like emitter with a microscopically enhanced electric field βE is given by

$J = A (\beta^2 V^2/\Phi d^2) \exp (-B\Phi^{3/2} d/V\beta)$

Where J is the current density, β is the field enhancement factor, Φ is the work function of the emitting material, E=V/d is the applied field, d is the distance between the anode and cathode and V is the applied voltage. In the terms A=1.54 x 10^{-10}A eV/V^2 and B= 6.83 x 10^9V/m $eV^{1.5}$. In the present study the field emission current density is cruelly estimated as J=I/A, where I is the field emission current and A is the surface area of the cathode πr^2 (r is the radius of sample = 0.4cm) (Fig.7) shows the results of field emission experiments. The calculated values for the onset field defined as the electric field required to draw a current of 0.1µA/cm^2 from the emitter and the turn-on field (threshold field) defined as the electric field required for 1µA/cm^2 is 0.31V/µm for copper.

According to the F-N model, a plot of $\ln(I/V^2)$ vs. $1/V$ (Fig.8) (known as F-N plot) has a linear behavior with a slope that can be used to evaluate the field enhancement factor as $\beta = (-6.83X10^9\Phi^{3/2})$/slope provided Φ is known. The calculated field enhancing factor ß is in the rage from 1,200 to 1,800. In particular, as clearly shown in Fig.7 the F-N plots can be easily fitted by straight line. The F-N Plot almost follows a linear relationship confirming the electron-tunneling through the potential barrier. The linearity of the plot indicates that the data satisfies the F-N relation.

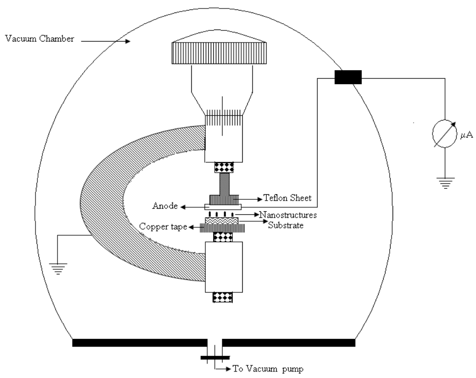

Figure 6: Schematic diagram of the experimental set-up used in field emission study.

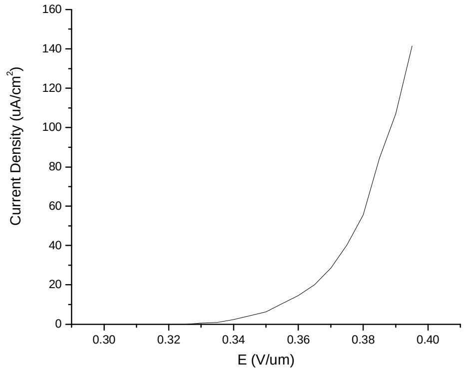

Figure 7: Emission current Vs applied voltage characteristics for electrodeposited copper nano wires

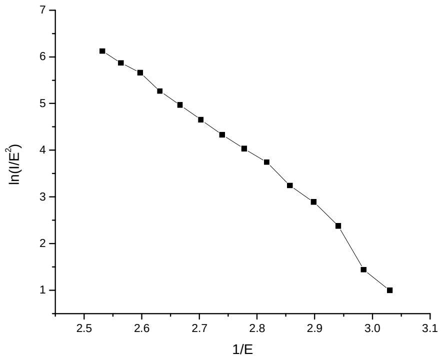

Figure 8 : Fowler-Nordheim plot for the copper nanowires.

4. CONCLUSION

Copper nanowires have been successfully fabricated into the nanopores of polycarbonate membranes through template synthesis via electrodeposition. Template synthesis is a simple and versatile method which we have used for the preparation of metal nanowires. The morphology of the fabricated nanowire arrays have been studied by using FE-SEM. XRD shows that the fabricated nanowires has crystalline in nature which possesses face-centered cubic structure and showing the most strong preferred orientation along (200) planes. The linear behavior of the wires has been observed from I-V characteristics. Field emission studies follow the linear relationship which indicates the electron tunneling phenomenon through the potential barrier. These nanowires find use in applications as interconnects in electronic device fabrication and as electron emitters in a television-like, very thin flat-panel display known as a field-emission display.

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