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ELECTRODEPOSITION OF COPPER NANOWIRES IN POROUS POLYCARBONATE MEMBRANES

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Copper nanowires of diameter 50 nm have been synthesized by electrochemical deposition in a nanoporous polycarbonate template. These membranes were created by ion irradiation of 30 μm thick polycarbonate foils at UNILAC accelerator of GSI, Germany. Subsequent chemical etching of these foils were carried out in PINSTECH using 6M NaOH solution at 50 ^{o}C. A thin Cu layer on one side of these membranes, deposited by thermal evaporation, acted as cathode. A Cu rod was used as anode and the deposition was carried out potentiostatically at room temperature in a two electrode electrochemical cell. Subsequent to fabrication, the wires were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and UV-Visible spectroscopy.

Keywords : Cu nanowires, Template method, SEM, XRD, UV-visible spectroscopy, Polycarbonate

1. Introduction

One-dimensional structures such as nanowires, nanorods, nanotubes, and nanobelts exhibit unusual behavior compared to their bulk counterparts, for example, the manifestation of quantum phenomena in the electron transport of metallic nanowires, [1] enhancement in the mechanical strength and hardness [2, 3], the interesting magnetic properties including giant magnetic resonance of nanowires [4], and decay of wires into chains of nanospheres stimulated by Rayleigh instability [5, 6]. These and other novel properties emerge as a consequence of reduced size of nanostructures and promise to be of major technological impact enabling new kind of devices and applications. In particular, nanowires are very suitable for investigating the dependence of physico-chemical properties on size reduction and are tipped to play an important role both as interconnects and functional units in future electronic, optoelectronic, electrochemical, sensoric, and electromechanical devices with nanoscale dimensions [4,7].

Conventional nano-fabrication techniques based on advanced lithographic methods, such as electron-beam or focused-ion-beam writing [8] and X-ray or extreme-UV lithography [4] reach their limits of downsizing due to available resolution. Further development of these techniques into practical routes to fabricate rapidly large quantities of nanowires from a diversified range of materials at reasonably low costs still require great ingenuity. However, chemical synthesis methods such as chemical vapor deposition (CVD), precursor decomposition, sol-gel chemistry, and electrochemical deposition provide an alternative strategy for generating nanowires in terms of materials diversity, cost, throughput, and potential for high volume production [4,7,9].

A straight forward approach used for nanowires synthesis is the so-called template method [7, 9]. This is a cost-effective, reliable, and versatile method to fabricate nanostructures and can be easily extended to synthesize nanowires of alloys as well as of multilayers [10,11]. In this method, prefabricated nanopores in a solid material are used as templates, and wires are created by depositing materials into the pores. Diameter and shape of the wires are predetermined by size and shape of the pores. Depending on the operating parameters, the deposited structure can acquire

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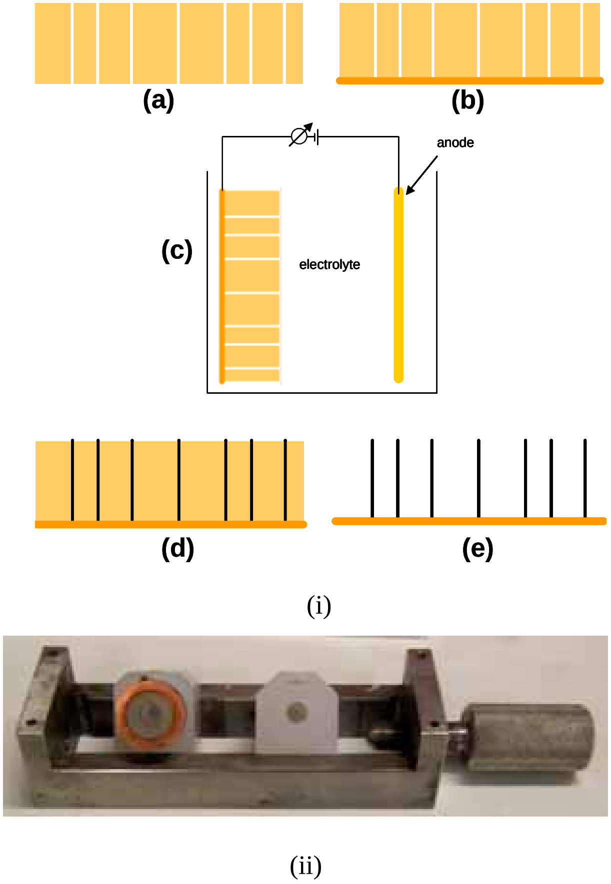
the shape of nanowire or nanotube. The most widely used templates are anodic alumina membranes and etched ion-track membranes (EITM) [9, 12, 13].

EITM make it possible to independently vary length, size, geometry and density of the wires. This technique offers a unique possibility of fabrication of single nanowires, which are subsequently reliably contacted and thus their properties are investigated independently [14,15]. EITMs are produced by a combination of swift heavy ion irradiation and chemical etching. When a heavy ion passes through certain materials, such as polycarbonate, it leaves a damaged zone along its path, the so-called latent track, which is selectively dissolved in a suitable reagent. This etching results in fine pores along the tracks, while leaving the rest of the material essentially unchanged. The pore diameters are controlled by the etching time. Insulating materials, for example polymers (polycarbonate, polyimide, and poly-ethylene terephthalate), mica and glass are used as templates. EITM with pore diameters as small as 10 nm have been fabricated in polymers and are commercially available [9, 16, 17].

Here we present our recent results on the synthesis of Cu nanowires in polycarbonate membranes. Copper nanowires are interesting due to potential applications in fields such as optoelectronics and sensorics and as interconnects in future nanoscale electronic devices [4,7]. For example, several recent works have been devoted to the investigation of surface plasmon polariton (SPP) waves of Cu nanowires on a substrate. The aim is to manipulate and transmit light on the nanoscale by exciting and guiding SPPs along metal/insulator interfaces [18].

2. Experimental

The steps involved in the synthesis process are depicted schematically in Fig.1 (i). Polycarbonate foils (MAKROFOL N, Bayer Leverkusen) of thickness 30 μm were irradiated with swift Pb heavy-ions of energy of 11.1 MeV/nucleon with fluence 1×10^8 ions/cm^2 at normal incidence at the linear accelerator UNILAC of GSI, Germany. Chemical etching was performed at 50 ^{o}C in a 6 M NaOH solution for 3 min. A thin Cu film was thermally evaporated on one side of these membranes to establish a conductive substrate for wire growth. This thin Cu layer was strengthened by subsequent electrodeposition of several μm thick Cu layer to provide mechanical stability to polymer films. The electrodeposition experiments were carried out in a purpose-designed two compartment electrochemical cell shown in Fig. 1 (ii). The electrochemical cell used in these experiments is a compression-sealed two electrode setup. The geometrical arrangement of the cell in combination with the materials employed for its construction provides a complete seal of the cell. This avoids losses of electrolyte, which may cause leakage currents during deposition. The galvanic deposition of Cu into the etched pores of the template was accomplished at room temperature with an electrolyte solution of 250 g/l $CuSO_4 \cdot 5H_2O$. The voltage applied was kept constant during wire deposition at 120 mV [19, 20].



(i)

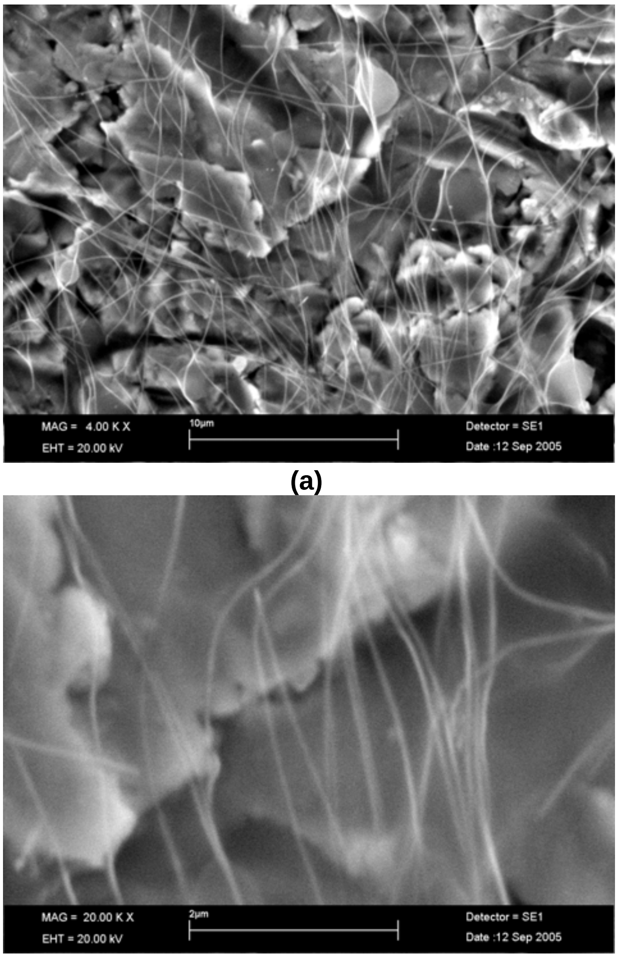
(ii)

Figure 1. (i) A schematic diagram of template method used in this work. (a) A nanoporous polycarbonate membrane (b) Deposition of a supporting Cu layer on one side of membrane (c) Electrochemical deposition setup (d) Electrodeposition of nanowires. (e) Dissolution of polymer to get free nanowires. (ii) Two electrode electrochemical cell used in this work.

XRD investigations were carried out while keeping the wires embedded in the template using the Cu-Kα_1 radiation. Cu baking layer was removed for XRD. SEM analysis of the wires was performed using LEO 4401 by dissolving the polymer in chloroform. The optical extinction spectra were measured in a standard transmission geometry mode, by removing both the evaporated and electrodeposited Cu back layers, using an UV-visible spectrophotometer (UNICAM, UV4). When performing the optical measurements, the corresponding blank polycarbonate template was used as a reference.

3. Results and Discussion

Low and high magnification SEM micrographs of Cu nanowires are shown in Fig. 2 (a, b). It is observed from these images that the wires bend into different shapes due to mechanical force experienced during the dissolution procedure and also break into segments of varying lengths. The wires possess in all cases cylindrical shape with smooth and homogeneous contours. The diameter, *d*, of the wires estimated from SEM micrographs is ~50 nm. Previously it was documented that the pore size in etched polycarbonate templates is determined by the etching time for particular etching conditions [19]. Since the same etching conditions are used in this study, using this previous published data we estimate that the pore diameter of the membranes used here is ~50 nm and this value conforms well to the values estimated from SEM. Since the electron mean free path is 39 nm for Cu at room temperature, we expect that quantum size effects will influence significantly the physical properties of copper wires with diameter 50nm. A pronounced resistivity increase has been observed for lithographically fabricated copper wires as narrow as 50 nm. This increase in resistivity can induce significant signal delay, which will degrade the advantages of nanodevices based on these structures. On the other hand quantum size effects in such small structures also influence rather significantly the optical absorption properties of these nanowires as discussed at the end of this section.



(a)

(b)

Figure 2. (a) Low and (b) high magnification SEM micrographs of Cu nanowires.

Figure 3 displays the X-ray diffractogram of as-deposited Cu nanowires. The XRD patterns were compared to the standard JCPD card number 040836. The inset in Fig. 3 shows the intensity distribution of an untextured polycrystalline or powder sample. The diffractogram of our wires shows the polycrystalline nature of these wires. The (220)/(111) and the (200)/(111) signal ratios are 0.3 and 0.6, respectively compared to 0.2 and 0.5 in a standard bulk powder sample (JCPD card number 040836), thus, pointing to a slight increase in 200 and 220 texture as compared to standard untextured Cu sample.

The texture coefficient (TC) formula given below was used to determine quantitatively the texture of Cu nanowires [21].

$$\mathrm{TC(hkl)}_i = \frac{\mathrm{I(hkl)}_i \big/ \mathrm{I_o(hkl)}_i}{\dfrac{1}{N}\sum_n \dfrac{\mathrm{I(hkl)}_n}{\mathrm{I_o(hkl)}_n}}$$

where $I(hkl)_i$ is the observed intensity of the $(hkl)_i$ plane and $I_o(hkl)_i$ is the intensity of the $(hkl)_i$ reflection of a standard sample. *N* is the total number of reflections taken into account. TC values larger than 1 indicate a preferred orientation of the wires and TC = *N* is the highest possible value indicating that all wires possess the same orientation.

The texture coefficients were calculated for this sample taking into consideration the intensities of the five reflections and amounts to 0.69, 0.86, and 1.01 for three low index fcc reflections, i.e., 111, 200, and 220, respectively. This show that the wires deposited under these conditions are polycrystalline and develop a weak preferred orientation in the $\langle 110 \rangle$ direction. This orientation is the preferred growth direction in the case of fcc metallic nanowires. Several groups have reported that potentiostatically deposited metallic nanowires such as Au, Cu, Ag, and Ni show preferential $\langle 110 \rangle$ texture at least at low diameters [22-26]. Thermodynamically, the growth of wires should satisfy the energy minimum principle. Recently Maurer et al. have demonstrated, theoretically, that the $\langle 110 \rangle$ texture is the preferred texture as it represents the configuration of lowest energy for fcc metallic nanowires [27].

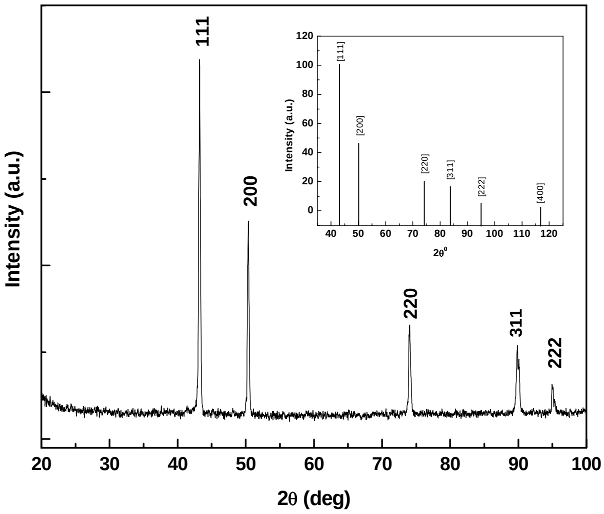


Figure 3. XRD patterns of 50 nm Cu nanowires. Individual reflections are indexed according to JCPD card number 040836. Inset shows the intensity distribution of an untextured polycrystalline sample.

The measured optical extinction spectrum of Cu nanowire arrays is plotted in Fig. 4. This was measured in such a way that the wire axis is parallel to the propagation direction of incident light, therefore, the direction of electric field vector is perpendicular to wire axis, as shown in the inset in Fig. 4. A strong optical extinction peak at 575 nm is clearly observed. This strong extinction can be explained by considering dipolar surface plasmon resonance (SPR). Recently Duan et al. measured the extinction spectra of Cu nanowires embedded in polycarbonate and they also reported a dipolar resonance peak at 590 nm wavelength for same range of diameters [28]. This electromagnetic resonance are one of the most characteristic features encountered in metal nanowires and is due to a collective oscillation of quasi free electrons in metallic nanostructures [29]. The resonance characteristics depend upon the shape, size of the material as well as the refractive index of the surroundings [30, 31]. Applications of surface plasmons include nano barcodes [32], metallic waveguides [33], surface plasmon assisted lithography [34], and surface enhanced Raman scattering. A blue-shift of the surface plasmon resonance with decreasing nanowire diameter is reported in literature [18, 28].

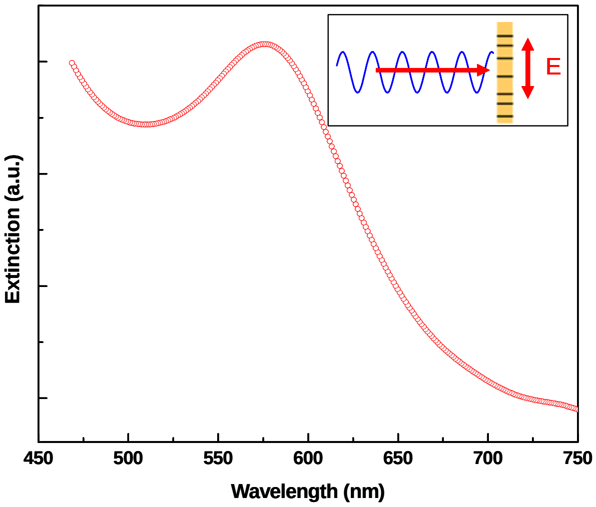


Figure 4. Optical extinction spectra of Cu nanowire arrays, Inset shows the experimental setup schematically.

4. Conclusion

Nanoporous polycarbonate membranes have been fabricated by chemical etching of ion-irradiated polycarbonate foils in 6M NaOH at 50 ^oC. Copper nanowires of diameter 50 nm were synthesized by electrochemical deposition in the etched membranes. XRD investigations show that the wires are polycrystalline with weak $\langle 110 \rangle$ texture. Optical extinction spectra of Cu nanowires show a strong surface plasmon resonance peak at 575 nm.

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