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Structural analysis of electrodeposited copper microstructures fabricated through template synthesis

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Abstract The electrochemical template synthesis of high aspect ratio copper microcylinders in the track-etch membranes of polycarbonate having nominal pore size of 800, 600 and 200 nm is considered. The morphological and structural analyses have been carried out through scanning electron microscopy and X-ray diffraction, respectively. The X-ray diffraction studies reveal that the material has FCC lattice structure with a high texture coefficient for (200) planes. Regardless of the nominal pore-size of the template membrane, the texturing has been found to decrease significantly when the electrolyte temperature during fabrication is increased from 30 to 60 °C.

Introduction

There is significant interest and ongoing research in the preparation and application of nanometer sized materials. The physical and chemical properties of these materials are quite different from those of bulk phase due to the high surface area to volume ratio. Their distinctive electronic, magnetic and optical properties contribute attractive prospects in the design of new electronic and optical devices, information storage, gas sensors, etc. [1]. A technique, suitable for structuring materials with small lateral dimensions and high aspect ratios, is the combination of heavy ion irradiation and chemical etching [2]. Compared to the broadly applied lithographic methods, the ion technique is characterized by the fact that each projectile creates an individual damage trail of a few nanometers in diameter. The length of the resulting ion track is determined by the ion energy and can reach several hundred micrometers. By chemical etching, these latent tracks can be developed to manifest as pores of different sizes and extremely large aspect ratios up to 10^4 [3].

These developed ion track membranes can act as templates for by electrochemical deposition of different materials into their pores. This is the basic idea of the so called template method [4, 5]. Template synthesis has been proved to be a versatile and simple approach for the preparation of nanostructures since the pioneering work of Martin's group [5, 6]. An attractive synthesis method, i.e. electrochemical deposition is controllable and inexpensive and provides great opportunities for the preparation of new materials and nanostructures [7–10]. Furthermore, electrodeposition is one of the most widely used methods to fill conducting and semiconducting materials into the template nanopores to form continuous nanowires. This patterned electrodeposition is a promising technique for fabricating nanostructures [11].

For our needle growth, we have selected copper as material because of its importance in the microelectronic industry. In the recent years, the submicrotechnology has started to replace aluminium with copper in microelectronic devices because copper has lower resistivity than aluminium, leading to faster devices and is also less vulnerable to electromigration.

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Electrodeposition of copper is the leading technology, since it has low cost, is fast, and is suitable for deposition in trenches of small dimensions and/or high aspect ratio [12].

Experimental, results and discussion

In the present work, Nuclepore polycarbonate membranes having pore size of 800, 600 and 200 nm, with a pore density of 10^8 cm^{-2} and 10 μm thickness have been used as templates for synthesis of copper microstructures through electrodeposition. In general, a suitable cell design is required. The layout design of such a cell along with other relevant details of the technique has been used previously [13]. Here, the electrodeposition of copper metal takes place through the pores, whose dimensions and geometry, therefore, dictate the morphology and geometry of the nascent microstructures thus produced.

Two-electrode electrochemical cell was used for copper deposition in the pores of the template. The cell is filled with freshly prepared and filtered electrolyte, i.e. 1.6 N (30 g/150 l) $CuSO_4 \cdot 5H_2O$ dissolved in double-distilled, de-ionized water at room temperature (35 °C), pH of the solution was adjusted to 2.14. The commercial electrolytes consist of an acidic copper solution containing specific additives, for instance brightening substances. Usually, these special agents are adsorbed at the cathode surface, increasing the electrode polarization and subsequently decreasing the grain size of the deposit. A high concentration of $CuSO_4 \cdot 5H_2O$ was used to supply a sufficiently large number of ions inside the pores during deposition. Sulfuric acid was added to increase the conductivity of the solution and to lower the cathode overvoltage. It is known that the cathode polarization decreases by adding a small amount of sulfuric acid.

The electrodepositions were performed potentiostatically at temperatures between 30 and 60 °C. The applied voltages were kept low to avoid side reactions such as hydrogen evolution. A current density of 8–10 mA/cm^2 was found to yield the most favorable results.

The cleaned and dried samples, were coated with a layer of gold palladium alloy in ''Joel, Fine Sputter JFC 1100'' sputter/coater, followed by mounting on specially designed aluminium stubs with the help of double-sided adhesive tape and viewed under ''Joel, JSM 6100 Scanning Electron Microscope'' at an accelerating voltage of 20 kV. Images were recorded on the photographic film in the form of negatives at different magnifications. Figure 1 shows SEM of the microstructures formed.

In order to confirm the crystalline quality of the deposits, the membrane containing nascent microstructures was peeled-off from the copper strip and X-ray diffraction of the deposited microstructures was carried out using D/Max Rint 2000 Rigaku

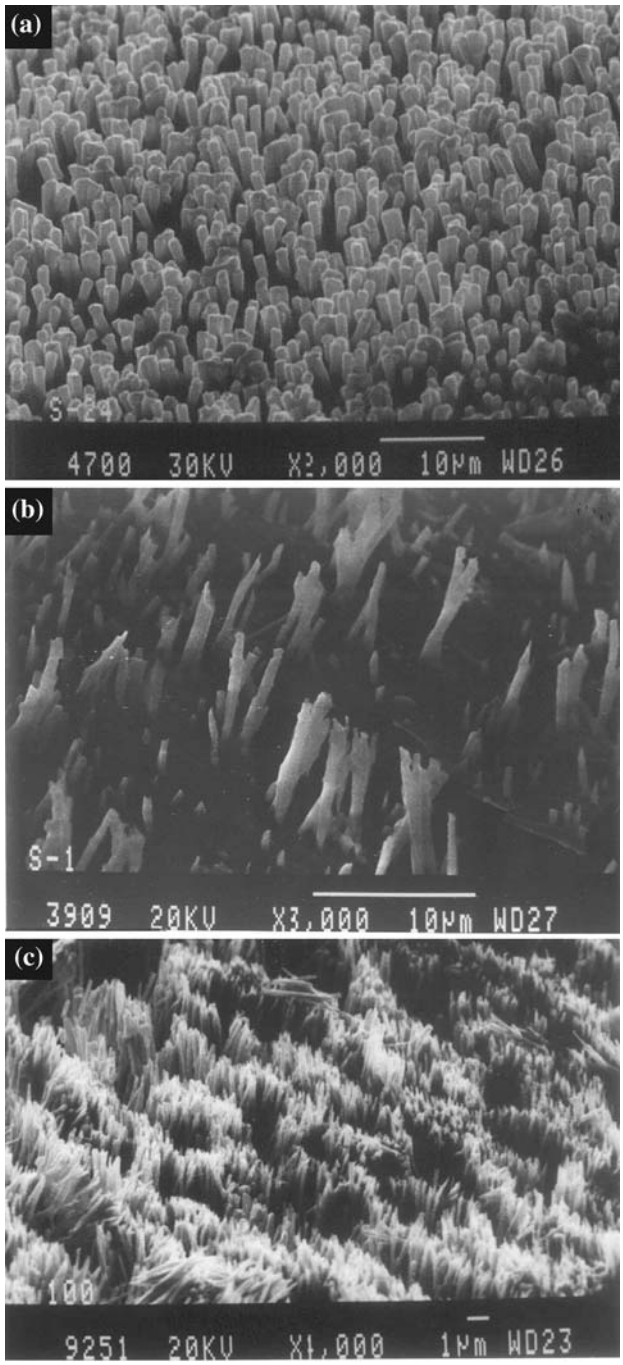

Fig. 1 Scanning electron micrographs showing (**a**) 800 nm, (**b**) 600 nm and (**c**) 200 nm diameter copper microstructures

(Tokyo) X-ray diffraction machine using characteristic copper wavelength of 1.5418 Å.

In all the X-ray scans (refer Fig. 2), four peaks have been obtained in the 2θ span ranging from 5 to 100°. Applying extinction rules, these peaks and associated *d*-values have been found to correspond to the copper *hkl* planes (111), (200), (220) and (311) as given in Table 1, thus confirming FCC structure of the microstructures formed. In case of the synthesized copper microstructures, the (200) plane is generally showing more prominence as compared to the standard random polycrystalline copper sample [14].

A comparison of observed peak intensity with standard copper specimen has been accomplished through Harris analysis [15], thereby obtaining the texture coefficients using the relationship given below:

$$P(h_i k_i l_i) = \frac{I(h_i k_i l_i)}{I_0(h_i k_i l_i)} \left[\frac{1}{n} \sum_{i=1}^{n} \frac{I(h_i k_i l_i)}{I_0(h_i k_i l_i)} \right]^{-1}$$

where *P(hkl)* is the texture coefficient of the plane specified by Miller Indices *(hkl)*; while *I(hkl)* and $I_0(hkl)$ are the specimen and standard intensities, respectively, for a given peak, and *n* refers to the total number of diffraction peaks considered.

The procedure for computing the texture coefficient is illustrated for one of the samples in Table 2.

Following a similar procedure, the texture coefficients were computed for all the specimens prepared at different temperatures. From the results given in Table 3, it can be observed that regardless of the size (diameter) of the microstructures, the samples prepared at room temperature generally show strong texturing for (200) planes, while this texturing is somewhat less prominent for samples prepared at higher temperatures.

As a check for the extent of texturing, the standard deviation (or coefficient of variance for that matter, since the mean of TC is always unity) of texture coefficients of the samples has been computed. It is observed that the dispersion (standard deviation) of texture coefficients is low for samples prepared at high temperatures. That is to say, for the copper microstructures prepared through template synthesis, the texturing can be reduced by increasing the temperature of electrolyte during electrodeposition. This observation can prove useful as it is generally much more difficult and challenging to produce microstructures that are not prominently textured [16].

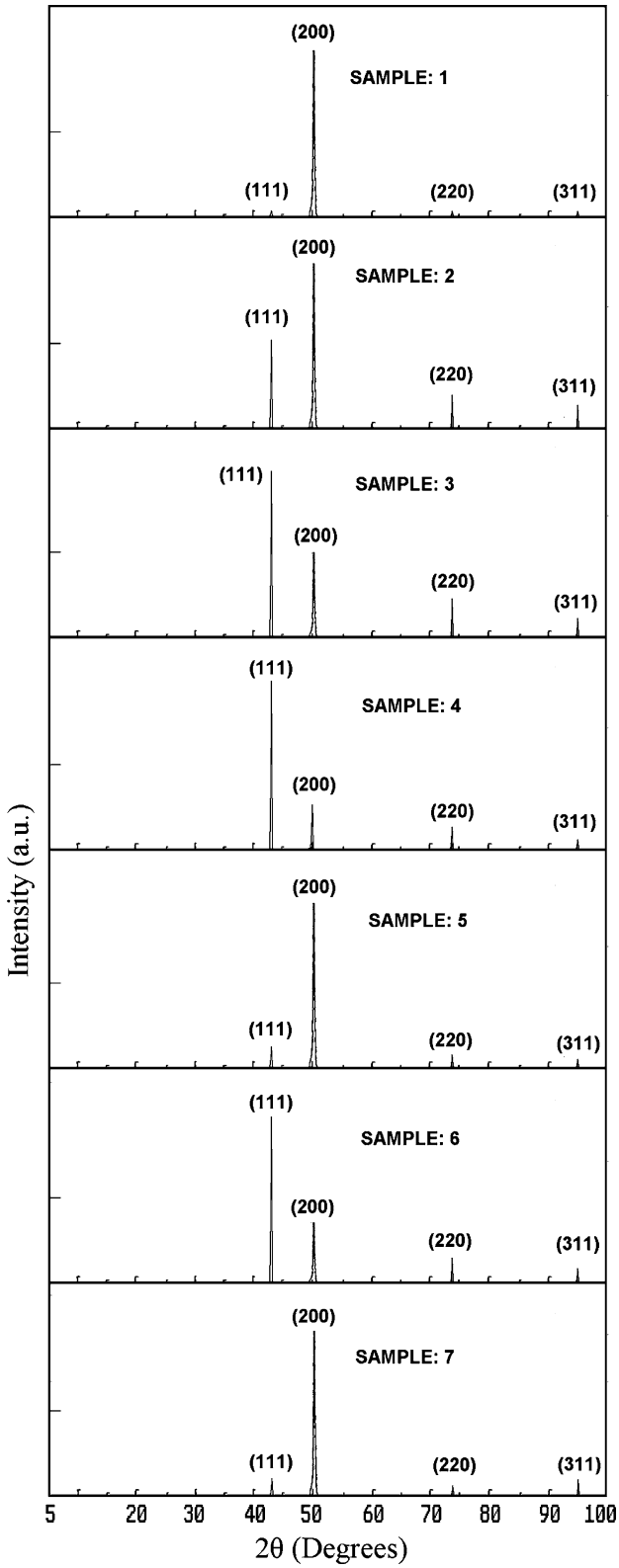

Fig. 2 X-ray diffractograms for the copper microstructures deposited at different temperatures

Table 1 Determination of lattice structure

2θ	$\sin\theta$	$\sin^2\theta$	Ratios	Normalized ratios	Lattice planes	*d*-Values (observed)
43.36	0.3694	0.1364	1.0000	3	(111)	2.0867
50.50	0.4265	0.1819	1.3333	$3.999 \approx 4$	(200)	1.8072
74.34	0.6041	0.3650	2.6748	$8.024 \approx 8$	(220)	1.2759
90.20	0.7083	0.5017	3.6765	$11.029 \approx 11$	(311)	1.0883

Table 2 Determination of texture coefficient

d values (Å)		*hkl*	Intensity		Texture coefficient *P(hkl)*
Standard	Observed		Standard I_0	Observed I	
2.087	2.0867	111	100	1980	0.24993
1.807	1.8072	200	67.8	16689	3.10709
1.278	1.2759	220	44.6	1247	0.35292
1.090	1.0883	311	41.3	949	0.29004

Table 3 Texture coefficients of specimens prepared at different temperatures

Sample number	1	2	5	7	3	6	4
Pore-size	800 nm	600 nm	200 nm	800 nm	800 nm	600 nm	200 nm
Temperature	30 °C	30 °C	30 °C	40 °C	60 °C	60 °C	50 °C
Hkl	Texture coefficient						
111	0.045	0.109	0.249	0.240	1.500	0.827	1.962
200	3.806	3.588	3.107	2.947	1.032	2.044	1.041
220	0.064	0.154	0.352	0.323	0.883	0.617	0.615
311	0.083	0.148	0.290	0.488	0.584	0.509	0.380
S.D.	1.871	1.725	1.405	1.302	0.382	0.708	0.697

Conclusions

Copper microstructures were electrochemically prepared by depositing into the micro pores of Nuclepore polycarbonate membranes having nominal pore size of 200, 600 and 800 nm. The morphology of the wires was verified through SEM.

X-ray diffraction studies confirm that the copper microstructure has an FCC crystal lattice. All the three specimens prepared at room temperature (30 °C) exhibit a strong texturing for (200) plane. It is further noted that regardless of the nominal pore-size of the template membrane, the texturing decreases significantly when the electrolyte temperature during fabrication is increased from 30 to 60 °C. These observations may help subsequent fabricators to exercise better control over texturing of the microstructures.

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