J MATER SCI 41 (2006) 3723–3728

Fabrication of copper microcylinders in polycarbonate membranes and their characterization

RAMINDER KAUR*, N. K. VERMA, S. KUMAR
Thapar Institute of Engineering and Technology, Patiala - 147004, India
E-mail: raminder_k_saini@yahoo.com
S. K. CHAKARVARTI
National Institute of Technology, Kurukshetra - 136119, India

The electrochemical template synthesis of high aspect ratio copper microcylinders in the track-etch membranes of polycarbonate having nominal pore size of 800 nm is considered. Effect of various parameters during electrodeposition is studied. It is found that only a narrow range of current densities yields good quality crop. Proper wetting of the membrane prior to electrodeposition is found to make significant contribution towards simultaneous start and uniform growth of the microstructures. The morphological and structural analyses have been carried out through scanning electron microscopy and X-ray diffraction respectively. It is observed that the actual diameter of the cylinders is slightly larger than the nominal pore-size. X-ray diffraction studies reveal that the material has FCC lattice structure with a high texture coefficient for (200) planes. Finally, the voltage-current studies have been carried out and the microstructures are found to obey ohm's law. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

The scientific and technological issues of nanostructured materials are currently attracting considerable attention. There are numerous methods for preparing nanomaterials. Several procedures have been proposed and applied to the synthesis of nanostructures, such as molecular beam epitaxy and microlithography. A technique used for the generation of replicas is known as template synthesis [1].

Heavy-ion radiation falling on a dielectric material such as a polycarbonate membrane leads to the formation of latent ion-tracks in the material. Due to their altered chemical properties, these latent tracks can be developed into through-pores by chemical etching. While the pore density remains dependent upon the radiation flux and exposure time, the pore-size and geometry can be controlled by varying the etching parameters of time, temperature, type of etchant and its concentration. The pore-density usually ranges from 10^7 to 10^8 pores/cm^2. These membranes can serve as templates for electrochemical deposition of nanowires. Since a wire acquires the exact pore shape, this template technique enables the fabrication of wires with different shapes viz. conical or cylindrical with dimensions down to a few nanometers.

Among the various methods used for fabrication of nanowires, template synthesis [2, 3] using electrodeposition has proved to be a low cost and high yield technique for producing nanowires. In this, the desired material is deposited within the pores of the nanoporous membrane. By template synthesis, the generated structures can be heterogeneous (including multi-layered) or homogeneous shaped as short squat fibrils, long needle-like fibrils, tubules, tapered conical (single or double cones) elements etc.

Depending on the pore size and geometry, as it is possible to exercise good control over the pore size in the membrane, this technique can be used for producing micro, as well as nano particles having monodisperse dimensions and geometry. The nanostructures thus obtained can either remain in the membrane or protrude as bristles on the cathode, or as free ensembles of nano/micro particles. The various parameters influencing the quality of electrodeposition include electrolyte composition, its concentration,

---

*Author to whom all correspondence should be addressed.

0022-2461 © *2006 Springer Science + Business Media, Inc.*
DOI: 10.1007/s10853-006-6262-z

pH, temperature, agitation and current density.

The technique of template synthesis was introduced by Possin, who used etched nuclear track filters of mica for preparing different metallic wires in pores as small as 40 nm diameter [4]. Thereafter, Williams and Giordano refined this method to obtain silver wires with diameters below 10 nm [5]. Successful synthesis of conducting polymers was demonstrated by Penner and Martin [6, 7]. Electrodeposition was carried out by Davis and Podlaha to fabricate metallic CoNiCu and Cu nanotubes in polycarbonate membranes [8]. Electrical properties of nanowires were studied by Enculescu *et al.* [9]. Crystallographically-oriented single-crystalline copper nanowires were fabricated by G. Riveros *et al.* [10]. Dobrev fabricated copper single crystal in pores of polymer ion track membranes [11]. Template synthesis for generation of nano/micro materials were carried out by Chakarvarti and Vetter [12].

Applications of template synthesis include arrays of field electron emitters, biosensors [13], synthesis of aqueous dispersions of monodisperse metallic colloidal rods [14].

In the present paper, the electrochemical synthesis of copper microwires in polycarbonate track-etched membranes obtained from Nuclepore is studied.

2. Experimental, results and discussion

Nuclepore polycarbonate membranes having pore size of 800 nm, pore density of 10^8 cm^{-2} and 11 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 [2]. 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 produced.

The cell consists of an acrylic housing capped with a removable cathode plate at the bottom. In order to make a copper cathode, a thin copper strip is cleaned with fine emery-paper to remove oxide scale, followed by wiping with cloth. It is attached to the cathode plate with the help of double sided adhesive tape in such a manner that the central portion remains in electrical contact with the cathode plate. Anode is made of a 25 mm diameter rod of copper suspended from the top-cover of the cell (Fig. 1).

The membrane is first rinsed with distilled water, partially dried and placed on the copper cathode strip—taking care not to trap any air-bubble. The amount of distilled water remaining on the membrane should be very small—just sufficient to wet the pores and help it adhere to the cathode. If this practice is not followed properly, two types of problems can arise. First, tiny air-bubbles and dry pores in the membrane reduce the effective area being electrodeposited, thereby affecting the calculations for total charge to be passed. Secondly, if a thick film of water is formed beneath the membrane, the latter may not come in contact with the cathode and so, the Cu^{++} ions that come through the pores undergo diffusion in the water-film prior to their reduction to Cu metal. This leads to the formation of a continuous layer rather than cylindrical microstructures.

The cell is then filled with freshly prepared filtered electrolyte, i.e. 2.5 N (200 g/l) $CuSO_4 \cdot 5H_2O$ dissolved in double-distilled, de-ionized water at room temperature (35°C). The solution has a pH of 3.14. No supporting electrolyte is used owing to high conductivity of $CuSO_4$ electrolyte.

Various current densities were applied, ranging from 65 mA/cm^2 down to 0.6 mA/cm^2. Large current densities are known to cause porous deposition. No microstructures were observed with current densities above 20 mA/cm^2. Current densities below 2 mA/ cm^2, on the other hand, resulted in the formation of regular, wedge-shaped crystals of the form shown in Fig. 2 and failed to yield cylindrical microstructures. Through iterative procedure, it was established that a current density of 8–10 mA/ cm^2 gave the most favorable results for deposition in 800 nm membrane. A number of current densities have been tried and it has been found that uniform crop can be obtained only in a narrow range of current densities. Whenever we get a si-

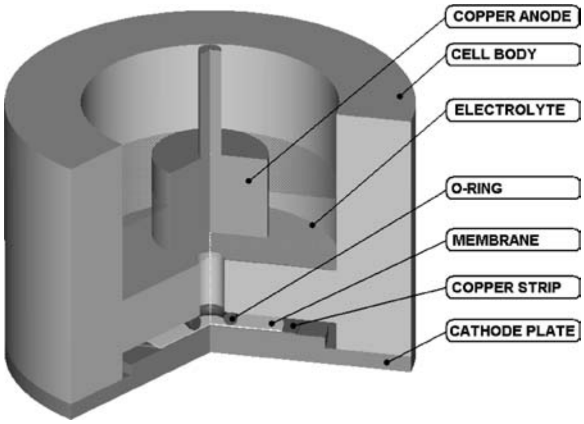

Figure 1 Section view of the electrochemical cell.

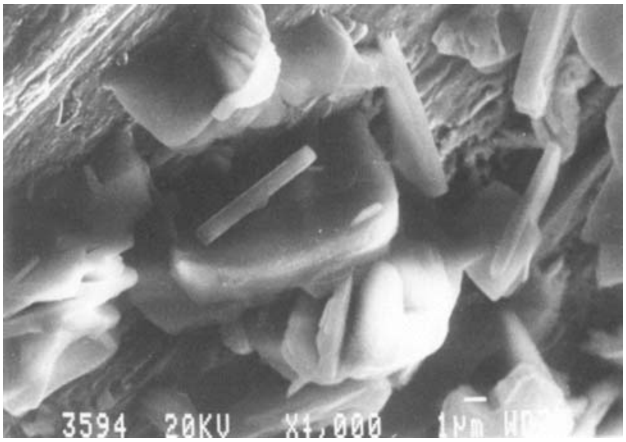

Figure 2 SEM showing the crystalline structures resulting from very low current densities.

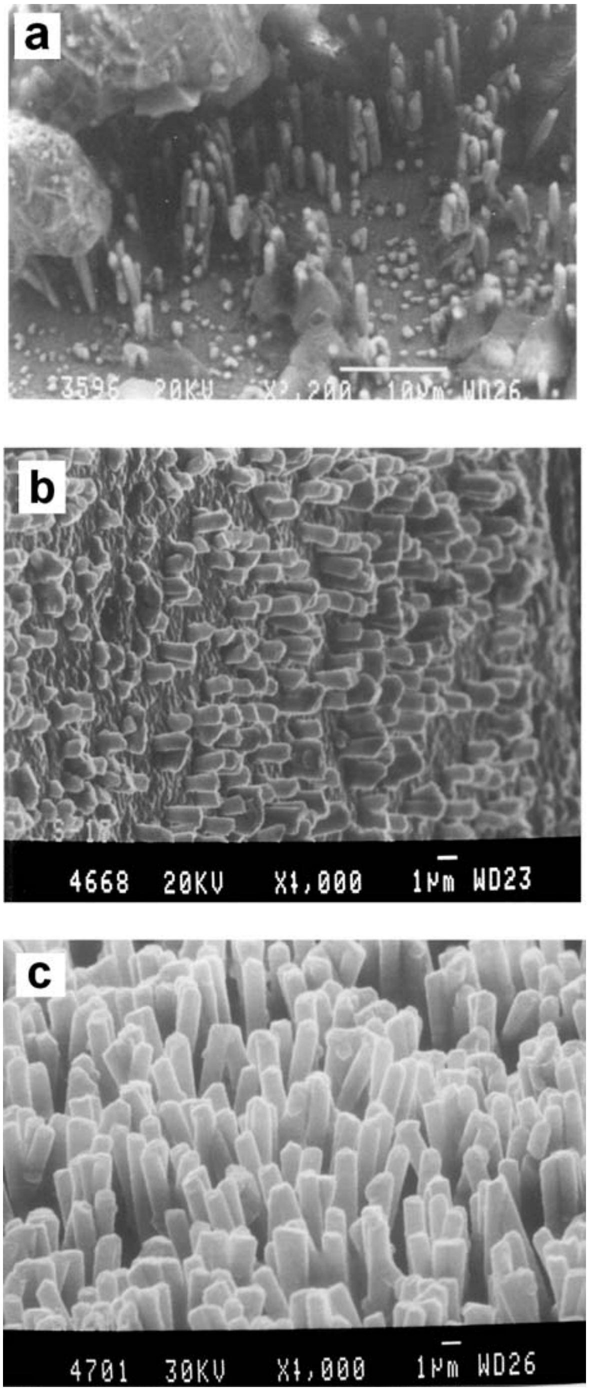

Figure 3 Scanning electron micrographs showing (a) intermittent deposition, (b) membrane dissolved at 25% of total time to pore-filling and (c) uniform crop of full-length microstructures.

multaneous start, uniform build up and 100% pore-filling, it is safe to assume a 100% current efficiency, as, otherwise, if hydrogen were evolved, then its bubbles would have clogged many of the pores, thus inhibiting further growth of microstructures in those pores.

During the course of experiments, it was found that wrapping the anode in a Whatman 42 grade filter paper proved beneficial by trapping the impurities generally present in commercial grade copper.

Many studies have reported an increase in current during deposition—relating the effect to completion of pore-filling, which leads to an abrupt increase in the area being electrodeposited [15]. However, no such increase in current was observed in the present work. Current flow was monitored for as long as three times the calculated time to complete pore filling, so that overdeposition was pertinent, but no noticeable change occurred. This observation can be explained on the basis of percentage membrane area under pores. In the present case, the nominal area under pores is over 50% of the total area, while in most of the studies citing an increase in current, the percentage area under pores was less than 4%. Accordingly, there is no substantial increase in area upon completion of pore-filling.

Upon completion of the pre-determined time for deposition, the current is stopped and electrolyte drained. The cathode plate is then removed, rinsed with distilled water and dried in air.

For the characterization of the synthesized microstructures by means of scanning electron microscope, the copper-strip along with the membrane is peeled-off from the cathode plate. In order to dissolve the polycarbonate membrane, the strip and membrane are placed in a dish containing small amount of dichloromethane. The dish is then slowly rotated to let the membrane come in contact with its solvent. In this manner, the microstructures are saved from any damaging hydrodynamic forces that might result if the dichloromethane were poured using a dropper. Upon dissolution, we obtain cylindrical copper microstructures standing upright on the copper strip in the form of bristles.

The cleaned and dried samples are subsequently mounted on aluminium stubs using double-sided adhesive tape, coated with a layer of gold-palladium alloy in Jeol, Fine Sputter JFC 1100 sputter, and viewed under Joel, JSM 6100 scanning microscope at an accelerating voltage of 20 kV and 30 kV.

Various micrographs given in Fig. 3 show the benefits of using a wet membrane. Fig. 3a shows SEM of the microstructures formed in a dry membrane. Regions where the electrolyte could not penetrate into the pores are devoid of any deposits, while some "late-starters" can be seen as underdeveloped tiny studs. The counter manifestation of this underdeposition is the overdeposition that can be seen towards top left corner. Fig. 3b shows an early stage during electrodeposition, where a wet membrane is applied. Here, the process was stopped when the pores were only 25% filled. The simultaneous start and uniform build-up of microstructures in a large percentage of pores can be seen. Such a process leads to a dense crop of equal, full-length microstructures such as those shown in Fig. 3c. In all the cases, however, the diameter of the microstructures has been found to be around 15–20% higher than the nominal pore-size. This is in agreement with the observations reported by many other studies [3].

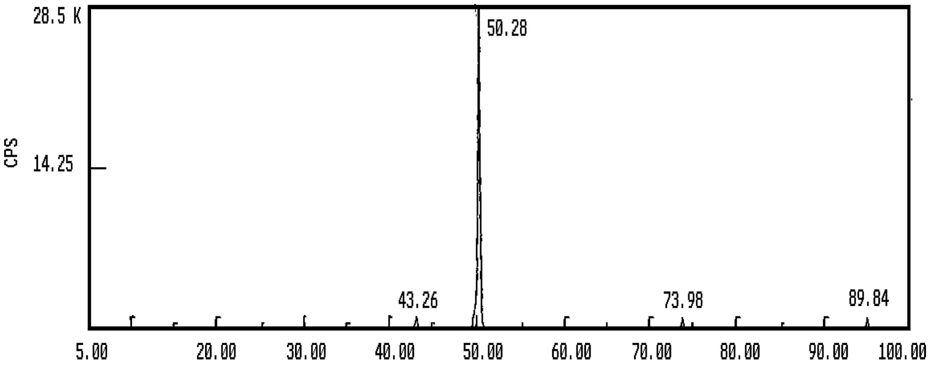

Figure 4 X-ray diffractogram for the electrodeposited copper microstructures.

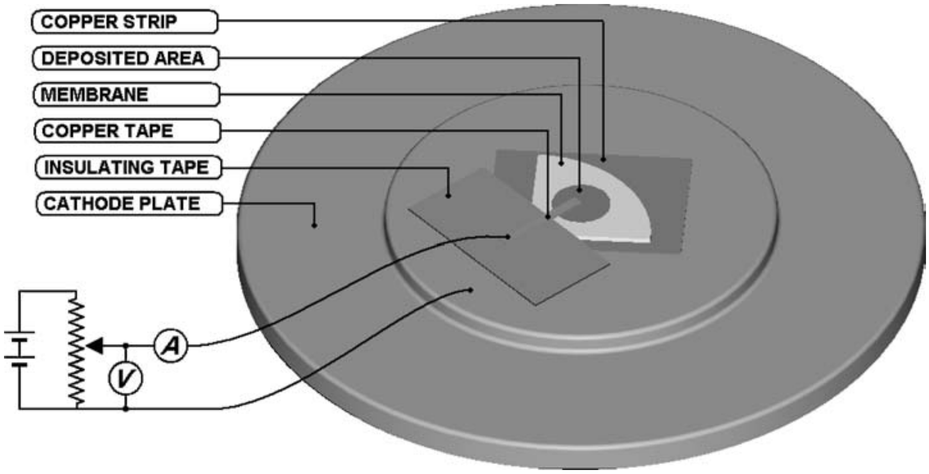

Figure 5 Setup for recording the V/I characteristics.

The transport of ions in a solution occurs either because of a gradient in the ionic concentration (diffusion), due to the movement of ions in an electric field (migration) or by convection. In our case, on applying electric potential, depletion of Cu^{2+} ions takes place at the cathode surface. This depletion results in a movement of ions from the bulk solution towards the cathode surface. In the first case shown in Fig. 3a, where a thick film of water is formed beneath the membrane, the latter may not come in contact with the cathode, and, so the Cu^{2+} ions that come through the pores undergo diffusion in the water film prior to their reduction to copper metal. In the second case shown in

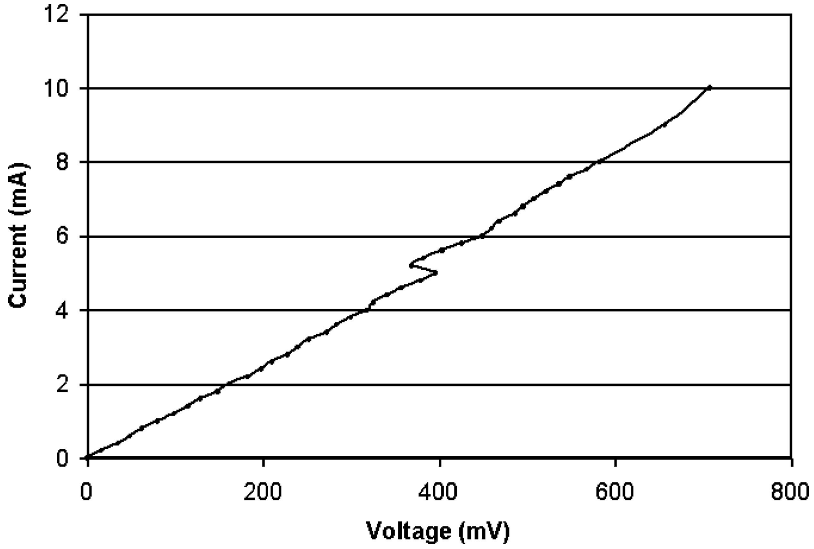

Figure 6 The V/I characteristics of 800 nm copper microstructure.

Fig. 3c, where the membrane is in direct contact with the cathode, no diffusion in the water layer has taken place, thereby leading to uniform growth of microstructures due to migration of ions.

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

Four peaks have been observed in the span ranging from 5° to 100°. Lattice planes corresponding to these peaks have been identified by applying extinction rules, as given in Table I. The ratios correspond to FCC lattice structure.

TABLE I Determination of lattice structure

2θ	$\sin\theta$	$\mathrm{Sin}^2\theta$	Ratios	Normalized ratios	Lattice planes
43.26	0.37	0.14	1.00	3	(111)
50.28	0.42	0.18	1.33	$3.98 \approx 4$	(200)
73.98	0.60	0.36	2.66	$7.99 \approx 8$	(220)
89.84	0.71	0.50	3.67	$11.01 \approx 11$	(311)

TABLE II Determination of texture coefficient

d values (Å)			Intensity		Texture Coefficient *P*(*hkl*)
Standard	Observed	*hkl*	Standard I_0	Observed I	
2.087	2.090	111	100	503	0.046
1.807	1.813	200	67.8	28413	3.807
1.278	1.280	220	44.6	317	0.065
1.090	1.091	311	41.3	378	0.083

A comparison of peak intensity with standard copper specimen can be obtained through Harris analysis [16], so as to obtain texture coefficient using the relationship given below:

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

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

The texture coefficients are given in Table II.

Note that the values for texture coefficient for (200) plane are greater than unity, while they are less than one for the rest of the planes. So, the microstructure is strongly textured in (200) planes.

In order to record the I–V characteristics, electrodeposition of the microstructures was carried out by placing the Nuclepore membrane on a thin sheet of copper, which in turn, was held in place on the cathode plate with the help of two thin strips of double-sided adhesive tape. Extra time was given for electrodeposition, so as to form over-deposition layer above the cylindrical structures, thus making it convenient to form electrical contacts with the microstructures beneath.

After completion of electrodeposition, the electrolyte was drained from the cell. The cathode plate was removed, carefully dip-rinsed with distilled water and dried in air. The dry membrane showed infinite resistance across its thickness and thus, made no contribution towards conductivity. An insulating tape was fixed adjacent to the electrodeposited area on the membrane, followed by a thin strip of copper tape that served as intermediate link for establishing electrical contacts with the fragile microstructures (Fig 5).

Voltage-current characteristics were then recorded using a potential divider as the source of variable voltage. Due to large range of voltages to be supplied, different scales of digital multimeter were to be used for measuring the potential difference across the microstructures. As smaller scales introduce larger resistance and hence, draw smaller current, the voltmeter was connected prior to the ammeter, so as to nullify the effect of different amounts of current drawn by it. The linear V/I graph shows that the microstructures obey ohm's law. The kink between the current values of 5.0 and 5.2 mA is as a result of the calibration differences in the mV and V scales of the Protek 506 digital multimeter used for measuring the voltage Fig 6.

3. Conclusions

In this paper, we have investigated in detail the electrochemical synthesis of copper microstructures using Nuclepore polycarbonate membranes as template. We conclude that the applied current densities during electrodeposition have a great influence on the quality of microstructures produced. Among a wide range of current densities, only a narrow window gave the most favourable results. In all the cases, the diameter of the nascent microstructures has been found to be 15–20% more than the nominal pore-size of the membrane.

Proper wetting of the membrane with distilled water has been found to have a very favourable influence in the form of simultaneous start and uniform growth of microstructures.

X-ray diffraction studies reveal that the microstructure has an FCC crystal lattice with a high texture coefficient for (200) planes.

A simple and convenient way is presented for determining the I–V characteristics of any microstructure prepared through electrochemical deposition. Besides, the applicability of Ohm's Law in the regime of 800 nm has been verified for copper.

Acknowledgment

We gratefully acknowledge the generous financial support provided by All India Council for Technical Education, Govt. of India, New Delhi, for this research work, vide their letter no. F.No.8020/RID/R&D-84–2001–02 dated 4/3/2002.

References

1. P. FORRER, F. SCHLOTTIG, H. SIEGENTHALER and M. TEXTOR, *J. Appl. Electrochem.* **30** (2000) 533.
2. C. R. MARTINE, *Science* **266** (1994) 1961.
3. C. SCHONENBERGER, B. M. I. VAN DER ZANDE, L. G. J. FOKKINK, M. HENNY, C. SCHMID, M. KRUGER, A. BACHTOLD, R. HUBER, H. BIRK and U. STAUFER, *J. Phys. Chem. B* **101** (1997) 5497.
4. G. E. POSSIN, *Rev. Sci. Intrum.* **41** (1970) 772.
5. W. D. WILLIAMS and N. GIORDANO, *Rev. Sci. Instrum.* **55** (1984) 410.
6. R. M. PENNER and C. R. MARTINE, *J. Electrochem. Soc.* **133** (1986) 2206.
7. Z. CAI and C. R. MARTIN, *J. Am. Chem. Soc.* **111** (1989) 4138.
8. D. M. DAVIS and E. J. PODLAHA, *Electrochem. Solid State Lett.* **8**(2) (2005), D1–D4.
9. I. ENCULESCU, Z. SIWY, D. DOBREV, C. TRAUTMANN, M. E. TOIMIL MOLARES, R. NEUMANN, K. HJORT, L. WESTERBERG and R. SPOHR, *Appl. Phys. A: Mat. Sci. Process.* **77** (2003) 751.
10. G. RIVEROS, H. GOMEZ, A. CORTES, R. E. MAROTTI and E. A. DALCHIELE, *Appl. Phys. A* **81** (2005) 17.
11. D. DOBREV, J. VETTER, N. ANGERT and R. NEUMANN, *Appl. Physics. A, Mat. Sci. Proces.* **69** (2) (1999) 233.
12. S. K. CHAKARVARTI and J. VETTER, *Radiat. Meas.* **29(2)** (1998) 149.
13. C. G. J. KOOPAL, B. DE RUITER and R. J. M. NOLTE, *J. Chem. Soc., Chem. Commun.* (1991) 1691.
14. B. M. I. VAN DER ZANDE, M. R. BOHMER, L. G. J. FOKKINK and C. SCHONENBERGER, *J. Phys. Chem.*
15. S. KUMAR, S. KUMAR and S. K. CHAKARVARTI, *J. Mat. Sci.* **39** (2004) 3249.
16. C. S. BARRETT and T. B. MASSALSKI, *Structure Metals Oxford: Pergamon* (1980) 204.

Received December 2004
and accepted April 2005