

SCANNING ELECTRON MICROSCOPY STUDY OF UNDOPED AND METAL DOPED ANODIC POROUS ALUMINA MEMBRANES

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ABSTRACT. Porous Al₂O₃ membranes were prepared by low-temperature anodic oxidation in aqueous electrolyte solution of Al foils with and without thermal pretreatment. Some of membranes were doped with Co and Ni by a.c. electrolysis. Scanning electron microscopy of the membranes confirms the existence of strain field regions, thus providing an experimental evidence of the earlier proposed mechanism for the development of the porous structure. The Co doped membranes were found as being very effective substrates for catalytic growth of carbon nanotubes.

Keywords: Porous Al₂O₃; Scanning Electron Microscopy; Carbon Nanotubes

1. INTRODUCTION

The obtaining of well-ordered nanostructured patterns with good accuracy over large areas is important task of the modern microelectronics. Utilization of substrates of naturally self-organized meso- or nanostructure can spectacularly reduce the processing times in comparison with conventional and electron beam lithography. Porous alumina prepared by anodic oxidation of aluminum has been recently studied and applied to produce nanowires, nanodots from different metals [1-3]. In this paper we report some of our results about the influence of the preparation conditions on the morphology of such alumina membranes, as well as some results obtained in the study carried out on electrochemically metallized membranes (doped by a.c. deposition of Ni or Co) in order to establish the dopant localization and structure. Alumina membranes doped with Co were tested as substrates for low-temperature catalytic growth of carbon nanotubes.

2. EXPERIMENTAL

Porous Al₂O₃ membranes were prepared from pre-annealed as well as thermally untreated 0.1 mm thick Al foils. Heat treatment was performed at 250°C or 300°C, and for 30 or 50 min, respectively. Low-temperature anodic oxidation was carried out in a two-compartment electrochemical cell, one compartment of which contained the aqueous electrolyte solution and the other distilled water. The Al foils were placed vertically between the two compartments providing their hermetic separation.

The exposed area of the Al foils was of 6 cm². An Al disk of 15 cm² area was used as counter electrode. In order to avoid the dissolution of the porous layer formed, during the oxidation the electrolysis compartment was cooled by circulating through a glass coil water chilled in a cryostat. However, the temperature slowly raised in time, from 4.0 ± 0.2°C at the start to 6.0 ± 0.5°C when the anodization was finished.

The preparation of the membranes was preceded by electrochemical cleaning ("polishing") of the Al foils, by anodic oxidation carried out for 2 min at 85°C and current density of 100 mA/cm² (used electrolyte: 70 % HNO₃ + H₃PO₄). Then, the foils were rinsed in distilled water, immersed for 5 min in 1 M NaOH, and carefully washed with bidistilled water.

Preparation of membranes by anodic oxidation was carried out in several steps as follows:

- (i) Oxidation at constant potential (10 V) for 10 min;
- (ii) Oxidation at constant current in 17 % sulfuric acid at current density of 15 mA/cm²; the time of oxidation was 90 and respectively 120 min for the different specimens;
- (iii) Oxidation at constant potential (20 V) for 15 min in 15 % sulfosalicylic acid;
- (iv) Finally, the samples were treated with 5 % H₃PO₄ in order to enlarge the pores and avoid their sealing.

The remained Al substrate was removed in a 0.1 M CuCl₂ solution prepared in 20 % HCl.

On some of the obtained Al₂O₃ membranes, Co or Ni was deposited by a.c. electrolysis. The deposition was carried out at 13 V and 40°C for 20 min using a metallization bath which contained 30 g/l CoSO₄, 40 g/l H₃BO₃ and 20 g/l (NH₄)₂SO₄ in case of Co deposition, and respectively 30 g/l NiCl₂, 40 g/l H₃BO₃ and 20 g/l (NH₄)₂SO₄ in case of Ni doping.

Carbon nanotubes were synthesized by low-temperature catalytic decomposition of a hydrocarbon over the Co doped alumina membranes. In this purpose, N₂ diluted acetylene was passed over the metallized sample for 10 min, the temperature ranging from 600°C to 700°C. The flows of the carrier gas (N₂) and of the reacting gas (acetylene) were set to 300 and 30 ml/min, respectively [4].

The surface morphology and cross-sectional structure of the samples were observed by means of SEM using a JEOL JSM 840 microscope. Microanalysis of metal doped membranes was carried out using ORTEC EDS equipment.

3. RESULTS

We have observed membranes in cross-sectional and in plan view. Micrographs in cross-sectional view show that oxidation produced columnar pores in all samples. In plan view all samples also show some common morphologic elements (plateaus, cracks, bulges). The size and number of morphologic elements is different in case of different preparation conditions. The formation of porous Al₂O₃ is accompanied by generation of strain fields at the interfaces between the substrate Al and the barrier layer of Al₂O₃ as well as between the Al₂O₃ and the electrolyte solution. This process is described in ref. [3]. Bulges find by us can be regarded as material evidence for the existence of such fields (see Fig. 1.). This supposition is confirmed by the finding of especially large number of bulges presented by non-annealed samples.

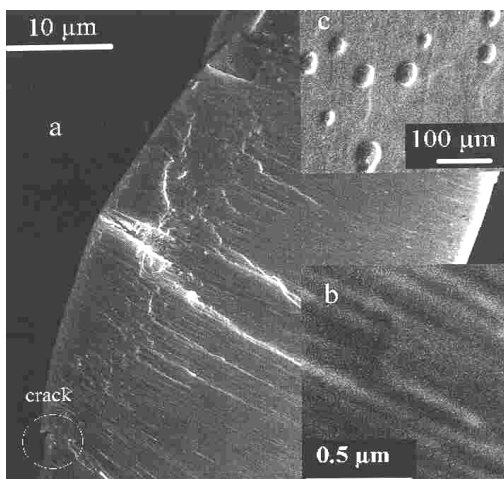


Fig. 1. Membrane morphology in case of non-annealed sample obtained by two-step anodic oxidation. Cross-sectional view: (a) bulge accompanied by cracks; (b) pores in higher magnification. Plan view: (c) bulges as they appear on the membrane surface.

Thermal treating of the Al foils influences the size of the formed pores: the average pore diameter in case of pre-annealed samples was of only 35 – 45 nm vs. 50 nm as measured in non-annealed samples (Fig. 2.).

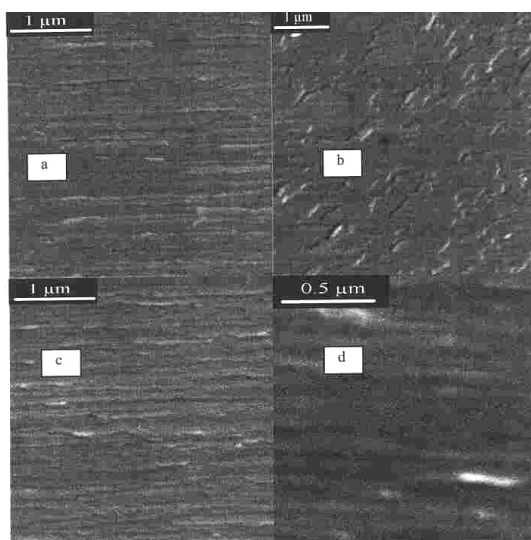


Fig. 2. Pores size in different samples. (a) Sample pre-annealed at 250°C for 50 min; (b) and (c) samples pre-annealed at 300°C for 30 min; (d) non-annealed samples.

The morphology of the examined samples was very "rich" and non-regular indicating a non-regular underlying porous structure: the columnar pores are not arranged in symmetrical hexagonal cells. However, as can be seen on Fig. 3., in some pre-annealed samples the plateaus observed form joint angles of approximately 120° in evidence of the "hidden" hexagonal symmetry. Open self-organized pores have been found exclusively in non-annealed samples (Fig. 4.).

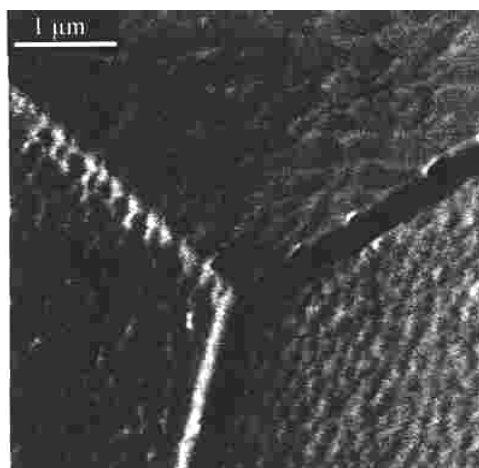


Fig. 3. plateaus formed on the surface of a sample pre-annealed at 300°C for 30 min, indicating a "hidden" hexagonal ordonation of the membrane structure.

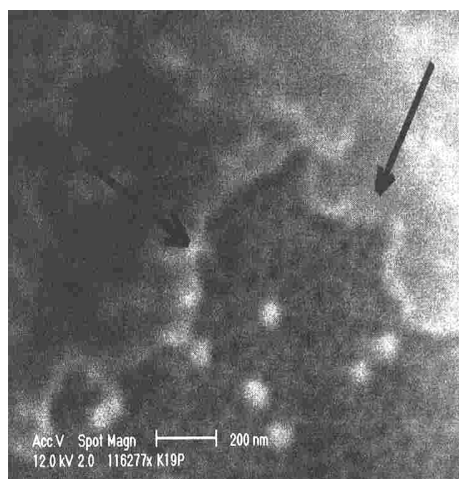


Fig. 4. Open pores domain on the surface of a non-annealed alumina membrane

A well-defined closure layer (the so called barrier layer) appears at the Al/Al₂O₃ interface (Fig. 5a.).

A similar continuous closure layer at the top of membrane (at the Al₂O₃/electrolyte interface) can be observed in case of pre-annealed samples only (Fig. 5b.).

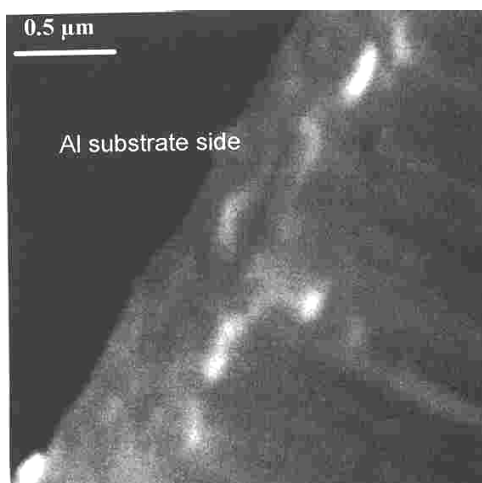


Fig. 5.a. Closure layer at the Al/Al₂O₃ interface in case of a non-annealed sample.

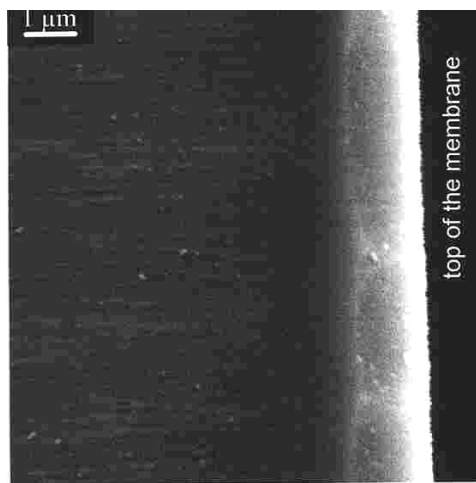


Fig. 5.b. Closure layer at the Al₂O₃/electrolyte interface (at the top of the alumina membrane) formed in case of a pre-annealed sample.

The metal penetration depth was determined by microanalysis on metallized samples. In non-annealed samples the presence of metal was detected in depth until approximately 4 μm . In case of pre-annealed samples, the deposited metal quantity was under the detection limit of the measuring apparatus: despite the visible presence of the metal, we were not able to evidence it.

The Co doped membranes were experimented, and proved to be suitable, as substrates for the purpose of catalytic growth of carbon nanotubes. As the catalytic activity was higher as expected, it was impossible to control the carbon nanotubes growing process even in the mildest experimental condition used (Fig.6).

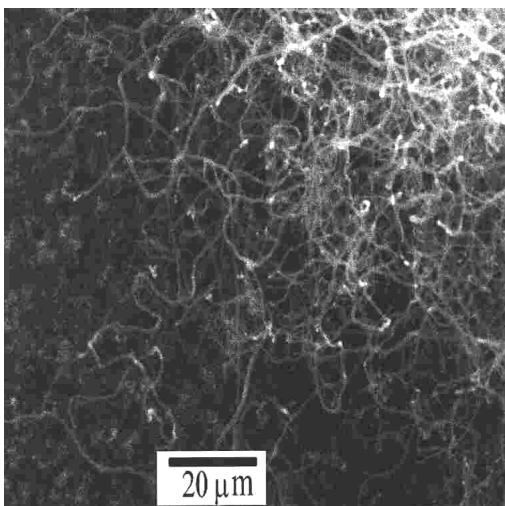


Fig. 6. Carbon nanotubes "scrub" grown on a Co doped non-annealed anodic alumina membrane.

4. CONCLUSIONS

The presented results can be summarized as follows:

- (i) the electrochemical oxidation procedure applied leads to formation of columnar pores even at low potential and short exposition time;
- (ii) pre-annealing seems to decreasing the strain field caused by the complex pore development process;
- (iii) the diameter of the formed pores can be influenced by the pre-annealing conditions (time and temperature of Al foils thermal treatment);
- (iv) carbon nanotubes can be grown in low-temperature conditions on similarly prepared Co doped samples in non-controlled way only.

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