

High aspect ratio self ordered alumina nanotubes, SEM and EDX characterization

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Abstract — Alumina nanotube and porous membranes were fabricated by anodic oxidation of 99.99 % aluminum foils in aqueous electrolytes containing orthophosphoric acids and nickel sulfate hydrate. This way, nanotubes and porous alumina membranes can be obtained in compact packing. Wall thickness, membrane thickness and pore diameter can be easily controlled by correct adjustment of solution composition, anodic oxidation time and the values of voltage and current applied. The membranes obtained as described are amorphous. The crystalline phases can be obtained as a result of a subsequent thermal treatment.

Index Terms — aluminum oxide nanotubes, porous aluminum oxide, anodic etching, XRD spectrum, high aspect ratio nanotubes.

I. INTRODUCTION

Electronics development nowadays greatly depends on the miniaturization of electronic components. Still today we are at a minimum that cannot be overcome using conventional production techniques. Hence, the development of new techniques is stimulated, among which is the utilization of dielectric or semiconductor templates as matrixes for the formation of new elements. An increased attention is paid to production of materials with self arrangement. When silicon porous membranes were obtained, the question whether other materials could be produced in an ordered porous form appeared. As a result of the research carried out by numerous research groups, the possibility to obtain nanostructures in semiconducting materials such as: Si, GaAs, InP GaN [1] etc., as well as in the oxides of different metals such as Al, Ti, Fe, Bi, Ni was proven[2]. Lately, the possibilities to obtain ordered nanostructured materials have attracted special attention.

Obtaining nanostructures based on aluminum oxide is of particular interest. Porous aluminum oxide membranes can be widely used as matrixes with the objective of producing nanostructured materials, nanowires for example, by means of electrochemical deposition. Another example of aluminum oxide utilization would be the creation of photonic crystals or random lasers.

Unlike the possibility to obtain aluminum oxide porous membranes, which was fully described in literature, the possibility to obtain aluminum oxide nanostructured tubular membranes up to the present is a major problem.

One way to obtain aluminum oxide nanotubes is reduced to the partial dissolution of the aluminum oxide wafer, of the pore walls in particular, creating an insulated nanotube.[3] Another method is based on the deposition of thin aluminum layers by electron beam evaporation on a Si substrate with a subsequent anodization and formation of a porous membrane[4].

II. EXPERIMENTAL PART

Aluminum oxide nanotubes with diameters between 20-40 nm have been produced using the procedure described below. In electrochemical experiments, Sigma Aldrich aluminum wafer with 99.999 % purity and 0.25 mm thickness was used. Initially, the wafer was degreased in acetone and washed in distilled water, after which, it was dried in a nitrogen flow. A $U=+40V$ voltage was applied to the aluminum wafer for a $t=1h$ duration, the temperature of the electrolyte was maintained at the value of $T=20^{\circ}C$. The concentration of the electrolyte is 0.03M nickel sulfate hydrate with 7 water molecules ($NiSO_4 \cdot 7H_2O$) of purum grade. During the experiment, the solution was stirred continuously. After etching for an hour, a $U=-100V$ voltage was applied to the sample to detach the Al_2O_3 membrane formed from the aluminum substrate. To open the tubes at both ends, the chemical etching method is used in a solution composed of 100 ml distilled water and 20 ml orthophosphoric acid (H_3PO_4) of chemically pure grade(xч), at the temperature $T=30^{\circ}C$ and etching period $t=5min$. As a result of these processes, tubes have been obtained with inner diameters 20-40nm and lengths of about 200 μm .

Aluminum oxide nanotubes with diameters of 100-150 nm have been produced using the following procedure. As initial material, aluminum wafer of 99.999% purity was used, 0.25 mm thickness, Sigma Aldrich. After degreasing in acetone and washing in distilled water, it is dried under nitrogen flow. A $U=+150V$ voltage is applied to the wafer for a period of $t=1h$ maintaining the electrolyte temperature around the value of $T=2^{\circ}C$. The electrolyte consists of a mixture of water and orthophosphoric acid 1M (H_3PO_4) of purum grade. The solution was continuously stirred. As a result of these processes, Al_2O_3 open tubes have been obtained with inner diameters of 150-270 nm and lengths of about 2.7 μm .

The experiments are carried out in a electrochemical cell made after the three electrode model, in which the platinum electrode serves as a counter electrode, and the

Ag/AgCl (1M KCl) electrode as a reference one. The potential between the sample and the reference electrode, as well as the anodic oxidation current was measured with Keithley digital multimeter.

The scanning electron microscope Vegatescan TS5130MM (SEM) equipped with chemical analysis EDX detector was used to analyze and characterize the samples.

III. RESULTS AND DISCUSSION

The parameters that influence the Al_2O_3 nanotube membrane formation process were analyzed as a result of several comparative investigations.

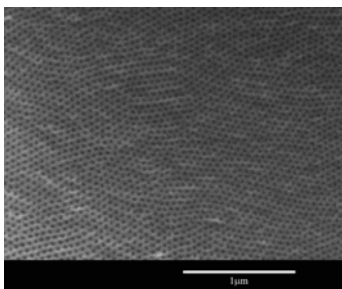


Fig.1. SEM image of an Al_2O_3 porous membrane

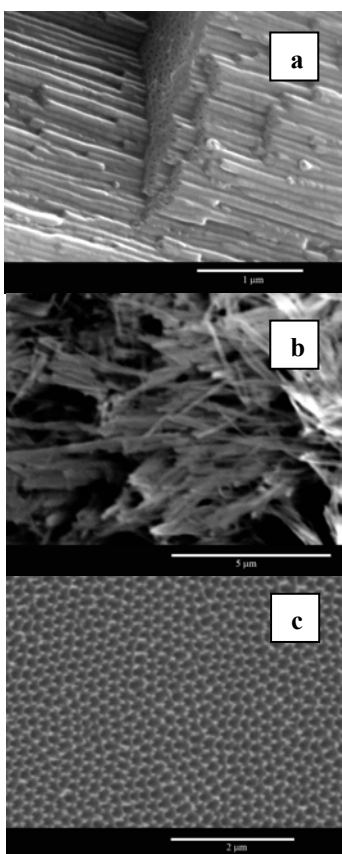


Fig.2. SEM images of an ordered tubular membrane of Al_2O_3 obtained in a solution containing a) 0.03M, b) 0.1M ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$); c) SEM image of the sample after the removal of the nanotube porous membrane.

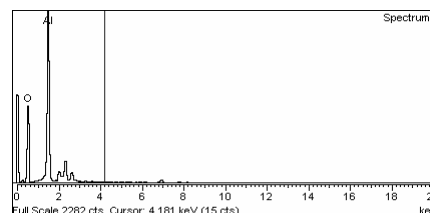


Fig.3. EDX spectrum of the nanotubular Al_2O_3 membrane obtained in the 0.03M ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$) solution.

Element	Weight%	Atomic%
O K	56.73	60.09
Al K	43.27	39.91
Totals	100.00	

Tab.1. The concentration of elements in the Al_2O_3 sample obtained in the 0.03M ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$) solution.

For the beginning, a number of experiments were carried out at the voltage of 40V, in solutions with different concentrations in the 0.01M and 0.3M interval. Starting with the concentration of about 0.01M the nanotube formation process takes place, but the distribution of tubes is extremely nonuniform, because the low concentration of ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$) is not enough for the creation of an ordered array of nanotubes. Uniformity is achieved in the case of 0.03M concentration Fig.2a, and the subsequent rise of the concentration leads to the acceleration of the etching and, ultimately, dissolution process of the nanotubes obtained with the formation of a filiform array Fig.2b, caused by the increased conductivity of the solution. In Fig.2c is showed the SEM image of the aluminum layer after the removal of the alumina nanotube membrane. The thickness of the tubes (80nm) as well as the inner diameter (30nm) of the tubes remain unchanged no matter what the ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$) concentration in the solution is. For lower voltages, the process of nanotube formation cannot be observed, while for higher voltages, an electrical breakdown and a rapid dissolution of the nanotubes takes place.

For the purpose of comparison, in Fig.1, the SEM image of an Al_2O_3 porous membrane with pore diameter of 30nm is presented.

In all of the experiments realized, besides the SEM images obtained, EDX analyses of samples were also carried out. In all cases the presence of the aluminum oxide is confirmed. The results of EDX analysis demonstrated that the chemical compositions of the samples obtained do not deviate from stoichiometry, see Fig.3 and Table 1.

As in the case of experiments realized in electrolytes containing nickel sulfate, a number of experiments with orthophosphoric acid at the voltage of 150 V in solutions with different concentrations between 0.6M and 2.5M were carried out. It is well known that at concentrations of about 0.2M - 0.4M H_3PO_4 and voltage of 120-130V, aluminum oxide porous membranes form (Fig.4) with pore diameter around 120nm, however, rising the voltage and the concentration of the orthophosphoric acid in the solution leads to the nonuniform formation of aluminum oxide tubular structures. The concentration at which the nanotube formation was observed is ca. 0.6M, but their distribution is

nonuniform, these being spread predominantly between aluminum oxide pores, the latter covering the big majority of the sample surface. Uniformity of tube formation is reached in the case of 1M concentration and $U=150V$ voltage (Fig.5a), the subsequent increase of the concentration leads to an acceleration of the etching and ultimately dissolution process of the nanotubes obtained. Increasing voltage to the value of 200V also contributes to the nanotube deterioration (Fig.5c). During the experiments no variation in the inner or outer diameter was observed.

In Fig.6 and Table 2, the results of the EDX analysis are presented demonstrating the presence of aluminum oxide. The chemical composition does not deviate from stoichiometry.

Analysing SEM images of the upper and lower parts of Al_2O_3 nanotube membrane, it was observed that in the case of the upper part the nanotubes are open, but in the case of the lower part they are closed. This fact is fully consistent with the nanotube formation theory described by several authors [5,6,7].

The length of the tubes greatly depends on the conditions of anodic oxidation. My observations showed that in time the nanotube formation rate decreases, which can be explained by the fact that solution depletion takes place at the electrolyte-oxide interface and a longer time is needed for the initial concentration of PO_4^{3-} ions to recover.

From the above-mentioned can be concluded that the factors that influence the Al_2O_3 nanotube formation and growth process are: electrolyte concentration, anodic oxidation time, anodic oxidation voltage. Like in the case of TiO_2 nanotube formation process by Mor et al., the Al_2O_3 nanotube formation process by anodic oxidation of Al wafers takes place in several stages: (1) formation of the oxide layer on the Al wafer surface; (2) pit formation in the oxide layer; (3) the growth of pits into pores; (4) oxidation and dissolution of metal parts between pores in the presence of electric field; (5) actual nanotube formation [5,7]. The team led by Gong suggested that nanotube structure formation as a result of anodic oxidation process is actually a result of the metal ion migration process from the regions between the pores to the oxide-solution interface. At high anodic oxidation voltages, the electric field is strong enough to mobilize the ions and their migration leads to cavity formation between pore surfaces which finally results in tubular structure formation [6].

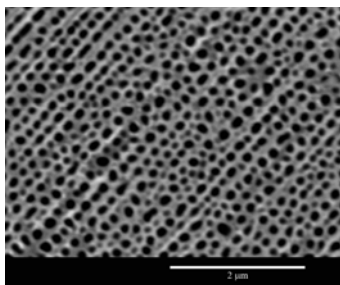


Fig.4. SEM image of an Al_2O_3 porous membrane obtained in a 0.25M H_3PO_4 solution.

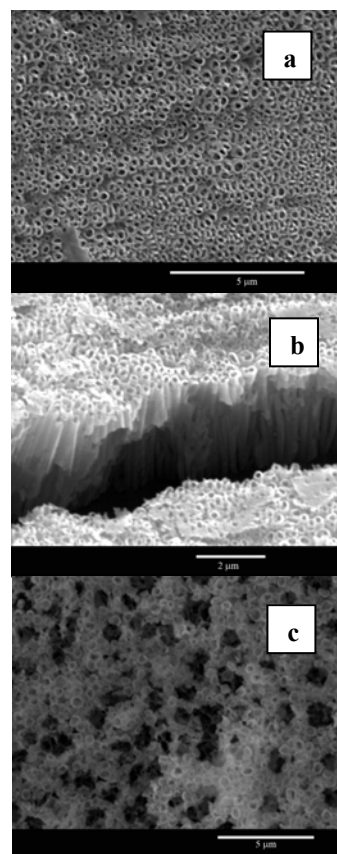


Fig.5. SEM image of an Al_2O_3 ordered nanotubular membrane obtained in a 1M H_3PO_4 solution at $U=150V$ a)top view; b)cross-section view; c) $U=250V$.

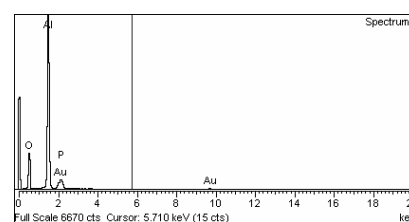


Fig.6. EDX spectrum of an Al_2O_3 nanotubular membrane obtained in a 0.25M H_3PO_4 solution.

Element	Weight%	Atomic%
O K	36.53	54.33
Al K	47.98	42.32
P K	2.28	1.75
Au M	13.21	1.60
Totals	100.00	

Tab.2. Element concentrations in the Al_2O_3 sample obtained in a 0.25M H_3PO_4 solution.

To observe the phase transitions taking place in the Al_2O_3 nanotubular membranes obtained in a 1M H_3PO_4 solution at $U=150V$, the samples obtained were subjected to thermal treatment at temperatures between 500°C and 1100°C. For these samples, XRD spectra were collected, the results being shown in Fig.7. For samples treated at the temperature of 500°C, it was determined that the nanotubes crystallize in $\gamma-Al_2O_3$ form. In the case of thermal treatment at the temperature of 700°C both γ and δ phases are present. For the temperature interval between 800°C and 900°C Al_2O_3 nanotubes crystallize into $\delta-Al_2O_3$ phase.

In the case of the sample thermally treated at 1000°C, both δ -Al₂O₃ and α -Al₂O₃ phases are detected. For the samples thermally treated at temperatures above 1000°C only the presence of α -Al₂O₃ phase was recorded.

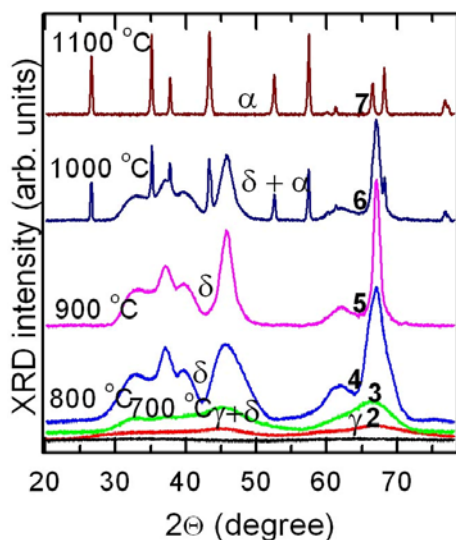


Fig.7. XRD spectrum for Al₂O₃ nanotubes obtained in a solution of 1M H₃PO₄ at U=150V after a thermal treatment at: 1 – not thermally treated, 2 -500°C, 3 -700°C, 4 -800°C, 5 -900°C, 6 -1000°C, 7 -1100°C.

IV. CONCLUSION

As a result of the study carried out, the process of aluminum oxide tube formation was investigated in aqueous solutions of (NiSO₄·7H₂O) and (H₃PO₄). It was observed that the tube formation process depends greatly on the electrolyte composition (pH) and the potential applied. Through a successful combination of these factors, membranes composed of close packed Al₂O₃ tubes were obtained. The Al₂O₃ membrane thickness increases with anodic oxidation time.

Applying a thermal treatment to the aluminum oxide nanotubular membranes, membranes with different crystallization phases can be produced. This fact can be widely used in optical resonators [8].

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REFERENCES

- [1] S. Langa, I.M. Tiginyanu, J. Carstensen, M. Christophersen & H. Föll. Formation of porous layers with different morphologies during anodic etching of n-InP. *Electrochem. & Sol.- St. Lett.*, Vol. 3, No 11, pp. 514- 516 (2000).
- [2] Sachiko Ono, Makiko Saito, Miyuki Ishiguro, and Hidetaka Asoh, Controlling Factor of Self-Ordering of Anodic Porous Alumina. *Journal of The Electrochemical Society*, 151(8) B473-B478 (2004)
- [3] Y. F. Mei, G. G. Siu, Ricky K. Y. Fu, P. Chen, X. L. Wu, T. F. Hung, and Paul K. Chu, Formation mechanism of alumina nanotubes and nanowires. *JOURNAL OF APPLIED PHYSICS* **97**, 034305 (2005)
- [4] Y.F. Mei, X.L. Wua, X.F. Shaoa, G.S. Huang, G.G. Siu, Formation mechanism of alumina nanotube array. *Physics Letters A* **309** (2003) 109–113
- [5] Mor G K, Varghese O K, Paulose M, Mukherjee N and Grimes C A. Fabrication of tapered, conical-shaped titania nanotubes *J. Mater. Res.* **18** 2588 (2003).
- [6] Macak J M, Tsuchiya H and Schmuki P. High-aspect-ratio TiO₂ nanotubes by anodization of titanium *Angew. Chem.Int. Edn* **44** 2100 (2005).
- [7] Varghese O K, Gong D, Paulose M, Grimes C A and Dickey E C. Crystallization and high-temperature structural stability of titanium oxide nanotube arrays *J. Mater. Res.* **18** 156 (2003).
- [8] Mihail Enachi, Viorel Trofim, Valeriu Coseac, I. M. Tiginyanu, and V. V. Ursaki. Structure and luminescence properties of porous alumina templates doped with rare earth elements and transition metals. Presented at 4th International Conference on Materials Science and Condensed Matter Physics, September 23-26, 2008, Chisinau, Moldova.