

THE INFLUENCE OF SUBSTRATE PREPARATION, ANODIZATION CONDITIONS AND POST ANODIZING TREATMENT ON AAO MICROSTRUCTURE

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Abstract

Series of anodization experiments was conducted on pure aluminium (99,95 Goodfellow) substrates with the aim to map the possibilities and evaluate available techniques. Oxalic acid electrolyte was used for anodization at different voltage levels ranging from 20 to 60V, while current was always measured continuously during the experiment. The influence of substrate surface treatment, time and grain size of the substrate was documented for as anodized oxide structures using FEG-SEM. Well aligned and evenly distributed pores of the diameters ranging 20- 35 nm were achieved. Extremely fine pores down to 10 nm were achieved using the step-down technique governed by current limitation. Further post-anodizing treatment was evaluated - pore widening by chemical and electrochemical etching, which resulted in pores 80nm wide.

The feasibility of electrodeposition of metallic wires directly into the AAO structure without substrate removal was evaluated. DC, AC symmetric and non-symmetric voltage setups were used. The deposition experiments results varied strongly depending on the post anodization treatment. For combination of pore-widening after anodizing with step-down stage, the deposition of copper nanowires was achieved. For simple step-down procedure, creation of very fine copper particles was realized using non-symmetric AC deposition.

Keywords: Anodic alumina, AAO, anodization, electrodeposition, nanowires

1. INTRODUCTION

Anodic aluminium oxide (AAO) materials are widely recognized as achievable templates for nanomaterials fabrication [1] [2]. Usually the standard route include polishing of the pure Al substrate, two anodization steps with removal of the first anodic oxide layer, which allows better self-organization of the pores [3] [4]. Then the substrate is removed by etching and the self-supporting oxide membrane is etched to achieve open pores. The electrodeposition of nanowires then is only possible after conducting layer of gold or similar metal has been deposited by PVD technique on one end of the pores [5] [6]. By this technique, nanowires of different compositions and different use have been prepared. [7] [8]

In this paper we report different anodization and post anodization treatment routes with the aim of preparing an AAO membrane on the Al surface that could be filled by metallic material using electrodeposition, without the need of removing the aluminium substrate. This would allow the production of self-organized metall-ceramic nanostructured composite on the surface.

2. EXPERIMENTAL

A 0.5 mm thin aluminium foil was used as the substrate, 0.2M water solution of oxalic acid was used as the electrolyte. Samples were at first chemically polished in the solution of 15 parts of concentrated H₃PO₄ and 85 parts of concentrated HNO₃. BK Precision 9122A served as the voltage supply. Annealing of selected samples was conducted at the temperature of 500 °C using Heareus tube furnace.

2.1 The anodization process

The first anodization was carried out under various voltages ranging from 20 V to 60 V, then the prepared oxide layer was etched away in the solution of 0,2 M phosphoric acid and 0,4 M chromic acid (in a 1:1 ratio). The second anodization lasting 10 minutes followed and was carried out under the same voltage as the first anodization. The diameter of pores and the thickness of the oxide layer changed with the voltage value, as showed in the **Table 1**. The difference between anodization at 20 V (a) and 60 V (b) is showed in the **Fig. 1**.

Table 1 Pore diameter and the thickness of anodized layer after the use of various voltage values

Voltage [V]	Pore diameter [nm]	Thickness of anodized layer [nm]
20	20	394
30	25	
40	30	960
50	35	1368
60	35	

2.2 Post-anodization treatment

The formation of electric contact between the aluminium substrate and an adequate pore diameter is important for the preparation of metal nanowires.

The pore diameter can be controlled not only by the voltage value but also by following chemical pore widening in 5 wt.% solution of phosphoric acid which etches the oxide structure and thins both the walls between the pores and the barrier layer as well. A cross view of the sample anodized under 40 V and subsequently chemically etched at the temperature of 35 °C for 10 minutes is showed in **Fig. 2a**. The pore diameter grew from the original 30 nm to approximately 80 nm.

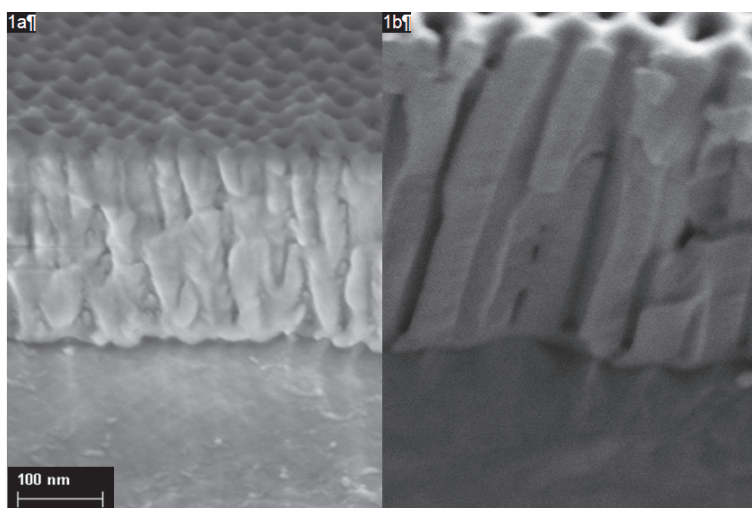


Fig. 1 Comparison of oxide layer prepared by anodization under the voltages of 20 V (a) and 60 V (b)

2.3 Post-anodization treatment

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Electrochemical pore widening in 0.2 M solution of KCl and voltage of - 5 V resulted in incomplete removal of the barrier layer. The best result (**Fig. 2b**) of this process was achieved after 5 minutes. The pore diameter was 90 nm and the wall between the pores was 20 nm thick.

2.4 Step-down anodization

Step-down anodization also influences the barrier layer thickness. This process is based on the fact that the pore diameter changes with the alteration of the anodizing voltage. The first anodization was carried out at 40 V for 5 minutes, then the voltage is raised to 60 V and the anodization continued for 5 minutes. The second anodization 60 V for 10 minutes was executed. A slow decrease in the current to its half value followed. The voltage started to decrease immediately after the change of the current. When the voltage reached a steady value, the current was reduced again. Thinning of pore diameter appeared with the decrease of voltage as shown in Fig.

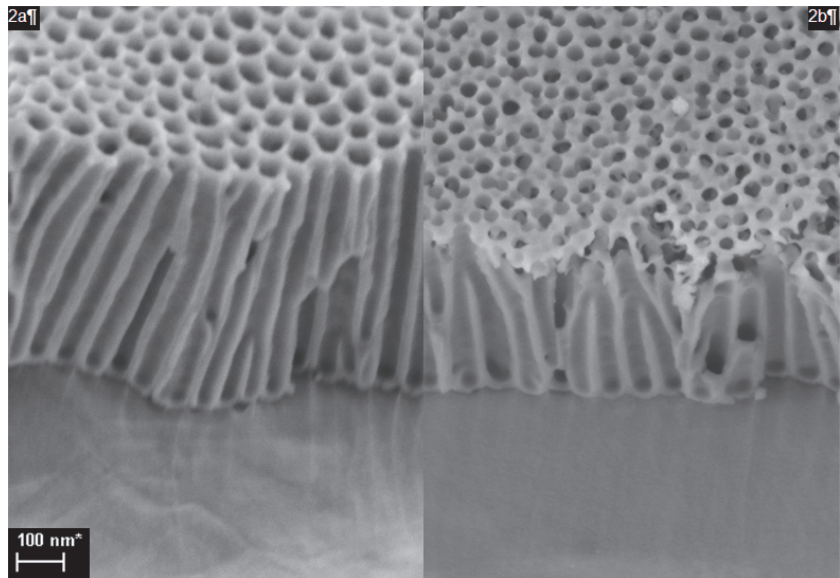


Fig. 2 a) Cross view of AAO after chemical pore widening, **b)** cross view of AAO after electrochemical pore widening

3. The barrier layer and the walls between the pores were thinned as well. However, the barrier layer was not removed completely.

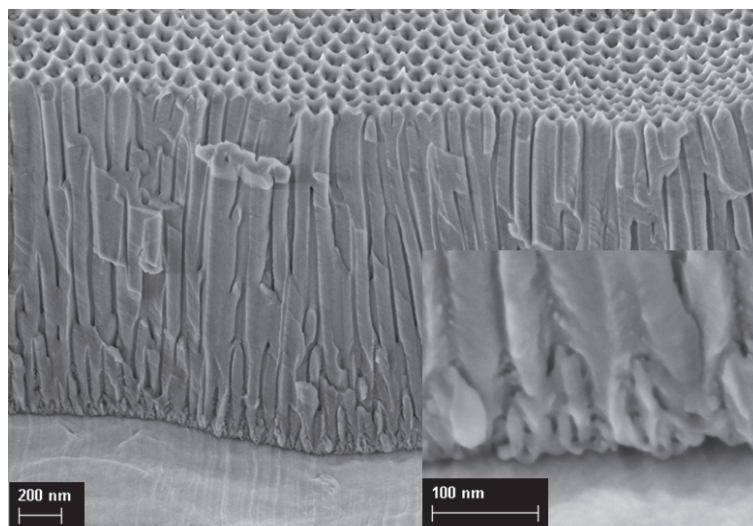


Fig. 3 Structure of AAO after step-down

2.5 The copper deposition

The electrolyte composed of 20 g H₂SO₄/l H₂O and 200 g CuSO₄·5H₂O/l H₂O was used for the copper deposition. At first DC was used for the deposition after the second anodization without any post-anodization treatment. Precipitates of impurities in the annealed material acted as a contact between the aluminium and the electrolyte. Copper nanowires were created near these defects at 2V deposition voltage despite empty pores in the rest of the AAO. Similar behaviour of annealed samples appeared after chemical and electrochemical pore widening - copper filled the pores influenced by the particles from metal impurities but

the rest of pores was left empty. Combination of step-down and chemical pore widening etched away the rest of the barrier layer. This way composite ceramic - metal structure (**Fig. 4a**) was achieved. Copper nanowires had a diameter of approximately 80 nm and a length of 2.5 μm . Copper was deposited in almost every pore and after removing the aluminium substrate and oxide matrix away by etching we got discrete copper nanowires as shown in **Fig. 4b**.

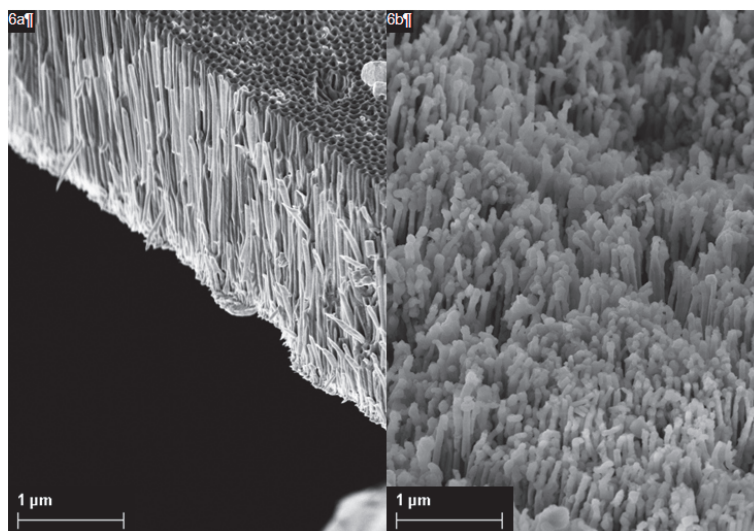


Fig. 4 a) Copper nanowires in oxide matrix, **b)** nanowires after etching oxide matrix away

However, this process is difficult to control and often the walls between the pores is removed during chemical pore widening so that copper is deposited under the oxide layer without creating any nanowires.

Subsequently step-down was conducted only till 10 V and chemical pore widening was fully omitted in next experiments. Copper was deposited by non-symmetrical AC of 10 V and the frequency of 50 Hz. This causes alternating charging and discharging of the barrier layer, which acts as a capacitor during the process. Positive charge is removed in each pulse which causes copper deposition; movement of cations inside the pores is possible. Using additional diode and resistance in the circuit we influenced the half period during which the barrier layer is being charged off.

Using this process for very short depositing times up to one minute population of small nanowires was created (**Fig. 6**). With longer times deposition times the deposited wires tend to dissolve again. This effect can be explained by chemical dissolution of the deposited copper as the consequence of a local change in the chemical composition of the electrolyte in pores or by deposition of cations to the barrier layer which causes electrochemical dissolution of nanowires.

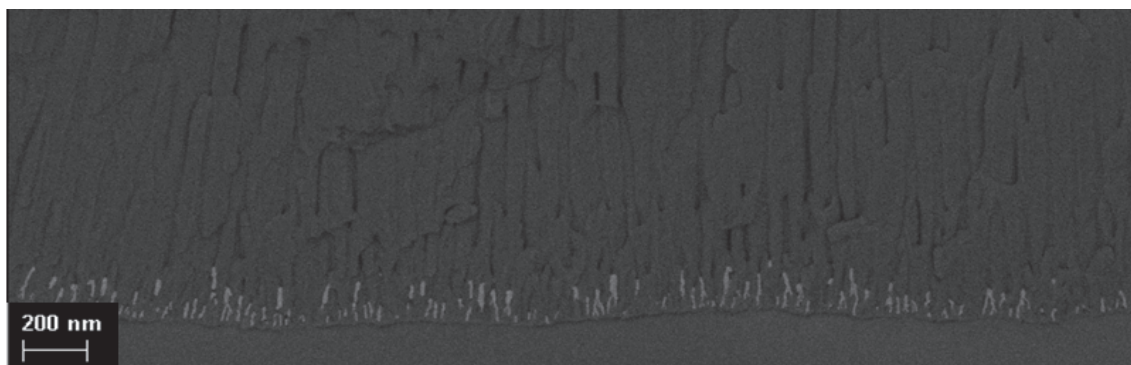


Fig. 6 Short nanowires prepared by non symmetric AC voltage

CONCLUSIONS

It is possible to control the diameter of pores through regulation of anodizing voltage during preparation of AAO. We can influence the pore diameter and thickness of barrier layer after anodization through chemical and electrochemical pore widening but it appears to be difficult to use chemical methods to create holes in the barrier layer. The only places where the copper was repeatedly deposited were impurity particles of iron which precipitated during annealing process in the material. This effect corresponds to common way of preparation of nanowires while using AAO as a matrix when the layer of metallic aluminium that should be anodised is supported by material such as titanium, which, when reached by the anodizing front, creates open bottoms for the anodic alumina.

We found the anodization with step-down procedure of reducing the voltage by halving the anodizing current as the best way for fabrication of AAO as a matrix for following electrochemical deposition of metals. Not only diameter of pores is reduced but also the thickness of barrier layer and walls between pores is reduced as well. The best result which was unfortunately hard to repeat was combination of step-down and pore widening. Barrier layer was completely removed and preparation of long nanowires on the whole sample was possible. We reached reproducible result while using step-down and alternative non symmetric voltage for copper deposition. We prepared very short nanowires in this way which dissolved with longer deposition time.

The next aim of our work is developing a method for preparation of long nanowires on the whole surface of sample.

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REFERENCES

- [1] Thompson, G.. Porous anodic alumina: fabrication, characterization and applications. *Thin Solid Films* 297, 192-201 (1997).
- [2] Ono, S., Saito, M. & Asoh, H. Self-ordering of anodic porous alumina formed in organic acid electrolytes. *Electrochimica Acta* 51, 827-833 (2005).
- [3] Montero-Moreno, J. M., Sarret, M. & Müller, C. Self-ordered porous alumina by two-step anodizing at constant current: Behaviour and evolution of the structure. *Microporous and Mesoporous Materials* 136, 68-74 (2010).
- [4] Han, C. Y., Willing, G. A., Xiao, Z. & Wang, H. H. Control of the Anodic Aluminum Oxide Barrier Layer Opening Process by Wet Chemical Etching. *Langmuir* 23, 1564-1568 (2007).
- [5] Jagminienė, A., Valinčius, G., Riaukaitė, A. & Jagminas, A. The influence of the alumina barrier-layer thickness on the subsequent AC growth of copper nanowires. *Journal of Crystal Growth* 274, 622-631 (2005).
- [6] Yuan, J. H., He, F. Y., Sun, D. C. & Xia, X. H. A Simple Method for Preparation of Through-Hole Porous Anodic Alumina Membrane. *Chemistry of Materials* 16, 1841-1844 (2004).
- [7] Alam, K. M., Singh, A. P., Bodepudi, S. C. & Pramanik, S. Fabrication of hexagonally ordered nanopores in anodic alumina: An alternative pretreatment. *Surface Science* 605, 441-449 (2011).
- [8] Sousa, C. T. *et al.* Tuning pore filling of anodic alumina templates by accurate control of the bottom barrier layer thickness. *Nanotechnology* 22, 315602 (2011).