An Approach for Nanostructuring of Piezoelectric Materials by Template-assisted Growth in Porous Aluminum Oxide

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This paper is devoted to the approach for nanostructuring piezoelectric materials to enhance their electrical signal producing ability from a small area of mechanical activation for potential application as energy harvesting. The geometrical structuring of the piezoelectric material leads to higher piezoelectric voltage per unit volume in comparison with a non-structured thin film. Template properties of porous anodic aluminium oxide (AAO) allow this approach. AAO layers with a variety of pore diameters (from 80nm to 100nm) were produced without overheating degradation of the substrates. The thickness of the studied layer was 19 1µm. It was realized sputtering of potassium niobate deposition into AAO to a maximum penetration of piezoelectric material into the pores. The obtained final structure was observed by scanning electron microscopy and Energy Dispersive X-Ray spectroscopy. The registered piezoelectric effect reaches to 454 mV for the reanodized membrane with pores widening. In this work, we continue to explore and further development of our previous research for template-assisted growth in porous aluminium oxide.

Introduction

During the last years, the trend for miniaturization of electronic devices to the sub-micron range has led to the rapid development of low power consuming, portable devices, requiring battery-free power supply from independent sources. The second most widespread type of alternative energy source after solar cells are piezoelectric harvesters. The small size of such elements, however, results is low energy conversion efficiency due to low electric power generated even at significant mechanical load [**1**]. To realize miniaturization without affecting the yield, the possibility for nanostructuring the piezoelectric materials have been intensively studied [**2**]. One-dimensional nanostructures, such as nanowires, nanoneedles, nanorods, etc. have been in the focus of the researchers from several years for application in all types of energy harvesting [**3-6**]. In this way, the total surface area of a material per unit of bulk volume will be greater, thus it is expected to enhance the piezoelectric charge. Additionally, due to the excellent alignment of the nanowires in the matrix, no external poling field would be needed. It is also expected that this type of structuring will concentrate internal stress, because geometrical structuring with specific shape can lead to the tailoring of the mechanical properties of any material [**7-9**]. Among the popular methods for synthesis of nanostructured piezoelectric materials are hydrothermal (limited mainly to ZnO nanowires and nanorods growth) and template-assisted by using anodic aluminum oxide (AAO) [**10**]. State-of-the-art covers material solution drop on the top of AAO membrane, template-assisted thermohydral growth and template-assisted electrodeposition growth [**11**]. Although the methods are simple and some of them low-cost, they are not conventional for the microfabrication technology and don't provide the possibility for wide range adjustment of the piezoelectric filler and wetting the template. Vacuum sputtering is conventional, as well as the control over the formation of the particles and delivering to the pores is greater, which could affect the filling degree. Different aluminium anodization modes are set to produce a variety of nanopores diameters and depth, to study the pores' size effect on the way of filling ability [**12**].

To the best of the authors' knowledge, there are no reports in the literature concerning the study of the piezoelectric response of AAO membrane filled by piezoelectric materials by radio frequency (RF) sputtering for potential applications as energy harvesting. This work aims to prove that this type of nanostructuring will improve the piezoelectric performance in comparison with a thin, dense (non-structured) film. This is assumed because the functional surface of the material increases after nanostructuring [**13**]. Comparison of the generating abilities of several elements, using different AAO templates is made based on the cross-sectional microscopic view and elemental analysis of the filled nanotubes, supported by oscillograms of the measured piezoelectric voltage. The obtained membrane elements with filled AAO nanotube arrays was produced at different modes exhibited satisfying values of the piezoelectric voltage in comparison with a dense, non-structured piezoelectric film on a substrate. The correlation between the AAO growth modes, nanopores dimensions, degree of filling and piezoelectric performance was demonstrated.

Experimental

Materials / chemicals details

For the AAO template preparation four aluminium substrates (S1, S2, S3 and S4) with 99.3% purity and dimensions 2x4x0.01cm were used. They were preliminary cleaned in a solution of 40% NaOH for 30 s at 30°C. To remove any natural oxidation all of them were additionally treated in a solution of 40g/l CrO_3 mixed with 90 ml/l H_3PO_4 at a temperature of 75° C for 20 min.

Characterizations/device fabrications /response measurements

The anodization was accomplished in 5% H_3PO_4 at 13°C, the anodization voltage varied from 100 to 150V and the anodizing time - from 10 to 130 min. The setup for growing AAO is shown in **Fig. 1** [14].

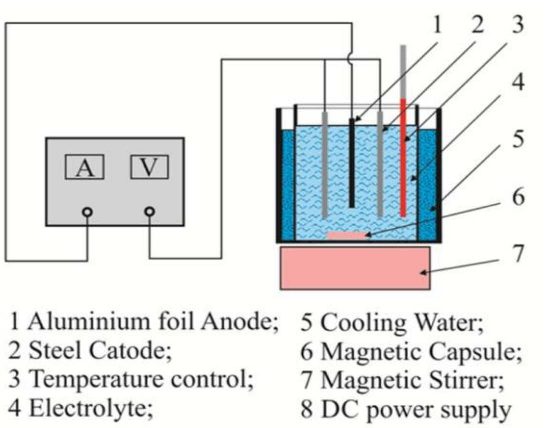

Fig. 1. Setup for aluminum anodization process, with technical components (from 1 to 8) [14].

AAO self-structured layers with variety of orderings were produced without overheating or degradation of the oxide layer at process conditions recommended elsewhere [**15**]. The suggested schematic diagram of the AAO nanotube array is shown in **Fig. 2(a)**. The structure as observed in **Fig. 2(b)** shows schematically the closed bottom sides of the nanopores. In **Fig. 2(c)** is the expected view of the nanopores walls at side cross-section. In **Fig. 2(d)** is shown the expected geometry and open end of the nanopores formed in AAO template after etching in CrO_3 +H_3PO_4.

The mechanical load was applied from laboratory made shaking setup by mounting on trapezoidal beam for uniform distribution of the dynamic stress along the whole sample independently of its area. Vibrations with frequency up to 50 Hz and equivalent mass load of 40 g were applied. Oscillograms were recorded with digital oscilloscope DQ2042CN. All electrical measurements were conducted at room temperature and open circuit.

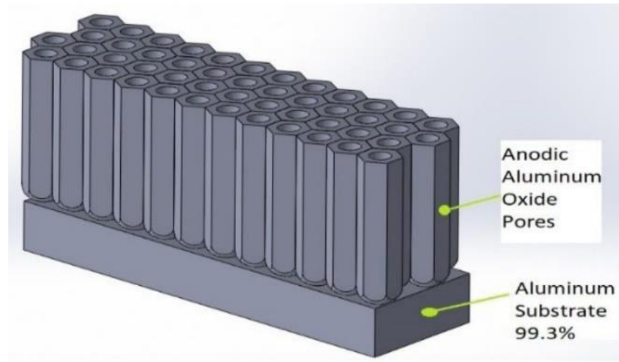

Fig. 2(a). 3D visualization of the substrate and the nanopores.

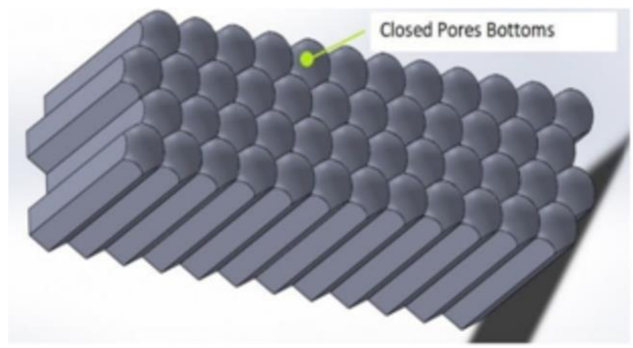

Fig. 2(b). Bottom side of the one end opened pores.

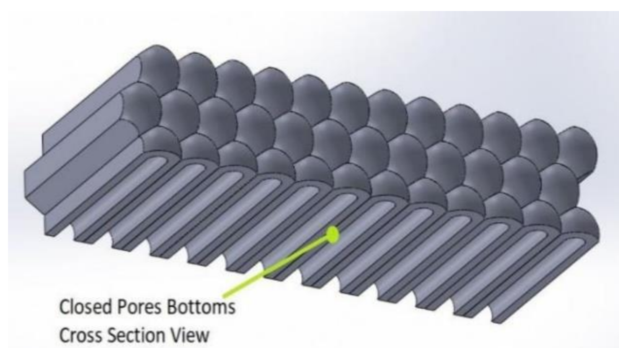

Fig. 2(c). Side view of the expected nanopores width and the separating walls.

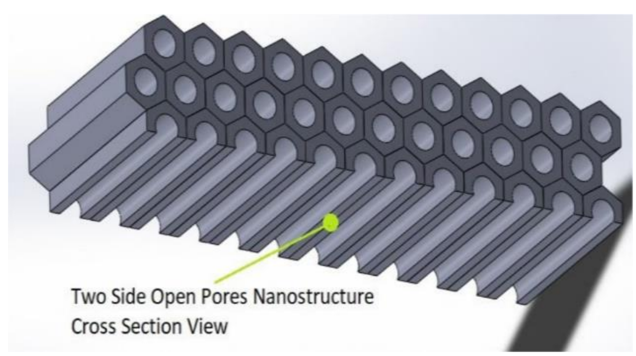

Fig. 2(d). The remaining AAO matrix with ability to promote vertically standing nanowires of piezoelectric materials.

Obtained membrane structure of the AAO after anodization and RF sputtering is shown in **Fig. 2(e)**. The middle ring-shaped formation is AAO membrane and due to the light refraction, it looks green-blue colored after filling with sputtered $KNbO_3$. The pores of the samples subjected to sputtering are two-side open.

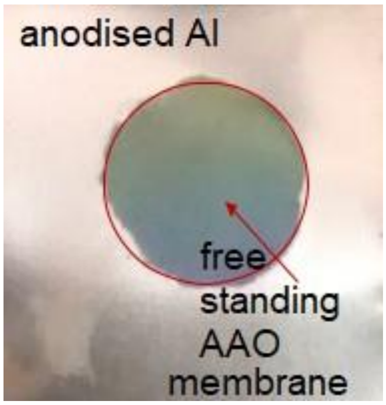

Fig. 2 (e). Membrane of filled by sputtering.

All pores bottoms were opened to obtain two-side porous, self-organized nanostructure [**16**]. Three variations of pores diameter were realized on the substrates. The first (S2) was submerged in an etching solution of 40g/l CrO_3 90 ml/l H_3PO_4 at a temperature of 60°C for 15s to expand the pores diameter. The second (S3) submerged in the same etching solution and temperature for 30s. The third variation (S1and S4) of the diameters of the pores is not treated with an etching solution. Two variations of reanodization (etching first deposed layer of AAO and repeating anodization) were realized on (S1 and S2) to compare reanodized AAO membranes with expanded and non-expanded pores. In our previous study, we established suitable sputtering conditions of potassium niobate to obtain successful filling, recommendable for the template of AAO [**14**].

Results and discussion

As a result, AAO structures (S1, S2, S3, and S4) were obtained with a thickness of 18 µm and penetration of piezoelectric material $KNbO_3$ in the pores from the two sides of the membrane. SEM images of the cross-section structures (S1, S2, S3, and S4) show the presence of niobium, due to the fact that brighter zones near the top sides of the pores represent the niobium accumulation. This shows that deposition of piezoelectric material on the inner walls of the pores is achieved.

Deposition parameters on substrate S1:

AAO membrane fabricated by:

- two-step anodisation at 100V and 13°C for 10 min with an intermediate etching of the oxide;
- protect anode contact area of the substrate with photoresist to prevent undercut;
- final anodisation at 150V and 13°C for 120 min;
- opening of pores bottoms with etcher CrO_3 +H_3PO_4;

On the first substrate, S1 where pores diameters were not increased it can be observed pores filling around 10% at depth of 1µm, and around 3% at the inner volume shown by element analysis.

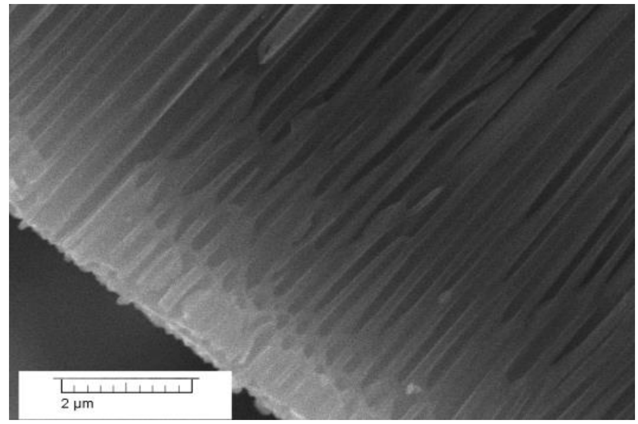

Fig. 3 (a). SEM image of AAO S1 membrane is observed penetration of piezoelectric material in pores volume (cross-sectional view) – **S1 Deposition.**

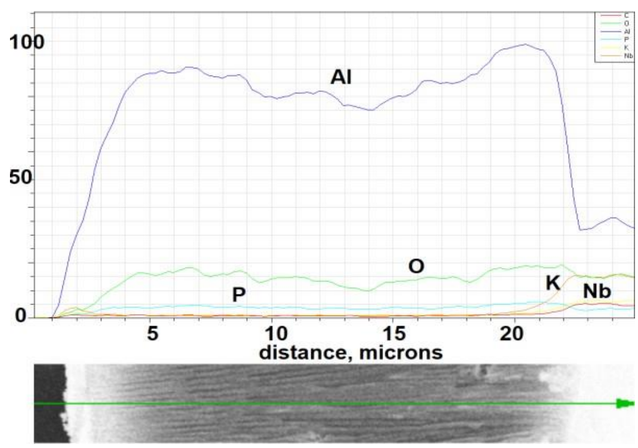

Fig. 3 (b). Elemental analysis of the membrane on S1 substrate.

In **Fig. 3(c)** is shown periodic electrical signal with effective value of the voltage of 362 mV, but there are distortions in the shape. This is probably caused by the accumulated piezoelectric layer on the surface of the pores witch forms irregular contact with the conductive layer.

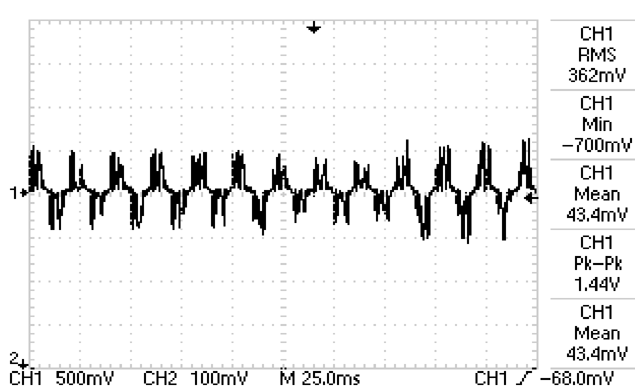

Fig. 3 (c). Piezoelectric signal from the membrane on S1 substrate.

Deposition parameters on substrate S2:

AAO membrane fabricated by:

- two-step anodization at 100V and 13°C for 10 min with an intermediate etching of the oxide;
- protect anode contact area of the substrate with photoresist to prevent undercut;
- final anodization at 150V and 13°C for 120 min;
- opening of pores bottoms with etcher CrO_3 +H_3PO_4;
- pores diameter expansion with CrO_3 +H_3PO_4 at 60° C for 15s.

For comparison, it was realized an experiment at the same conditions but with additional expanding of pores diameter S2. From the SEM images it is noticeable that the piezoelectric material has better penetration on reanodized membranes and nanotube structure is better ordered compared to S1.

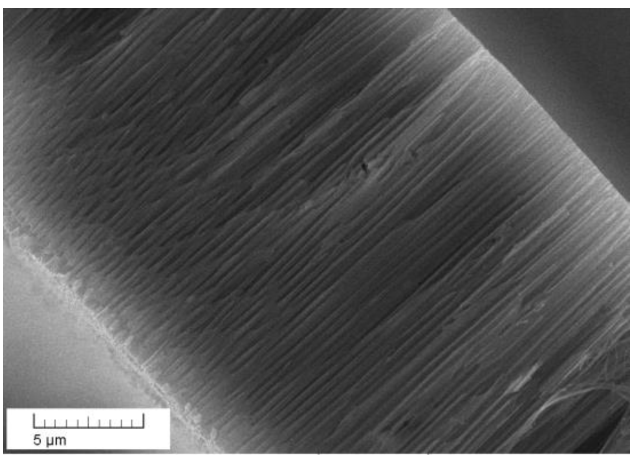

Fig. 4 (a). SEM image of AAO S2 membrane is observed penetration of piezoelectric material in pores volume (cross-sectional view) - **S2 Deposition [14].**

Fig. 4(a) is SEM image of AAO S2 membrane, where penetration of piezoelectric material in the volume of the pores (cross-sectional view) is observed [**14**]. In **Fig. 4(b)** was visualized the elemental analysis at maximum penetration rate of the piezoelectric material - around 15% from two sides at depth of 1µm, and around 4% at the inner volume.

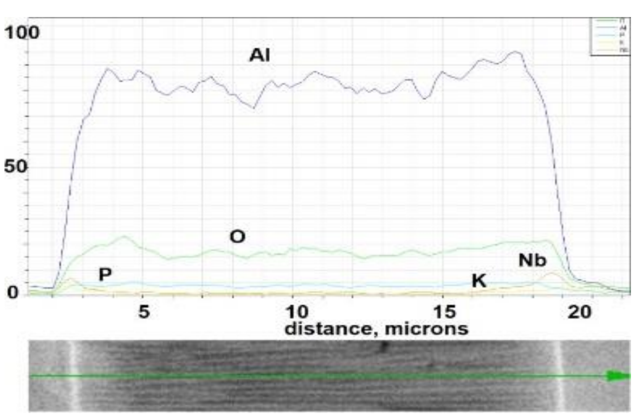

Fig. 4 (b). Elemental analysis of S2 penetration depth of the piezoelectric material in the inner volume of AAO [14].

The electrical measurements result shows stable piezoelectric voltage as a function of the time. The membrane S2 produced voltage of 454 mV which is the highest voltage from all four membranes. This proves the highest quantity of the piezoelectric material in the structured AAO matrix.

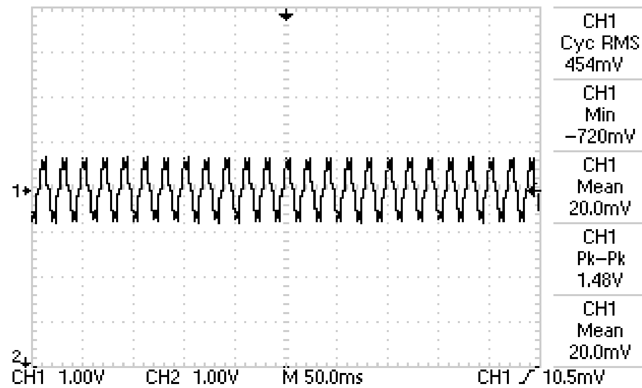

Fig. 4 (c). Elemental analysis of S2 penetration depth of the piezoelectric material in the inner volume of AAO [14].

To confirm results on S1 and S2 there were realized two more samples S3 and S4 without reanodization. Obtained SEM, elemental analysis and electrical measurements confirmed that the main factor for optimal pores filling is reanodization and the second one is the diameter of the pores.

Deposition parameters on substrate S3:

AAO membrane fabricated by:

- one-step anodization at 100V and 13°C for 10 min;
- protect anode contact area of the substrate with photoresist to prevent undercut;
- final anodization at 150V and 13°C for 120 min;
- opening of pores bottoms with etcher CrO_3 +H_3PO_4;

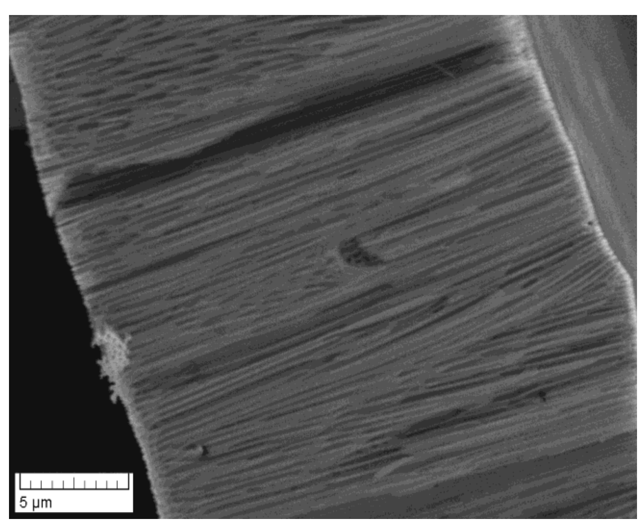

Fig. 5 (a). SEM image of AAO S3 membrane is observed penetration of piezoelectric material in pores volume (cross-sectional view) - **S3 Deposition**.

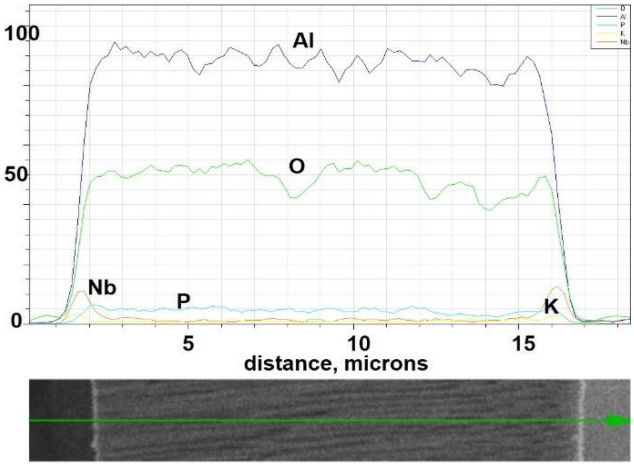

Fig. 5 (b). Elemental analysis of the membrane on S3 substrate.

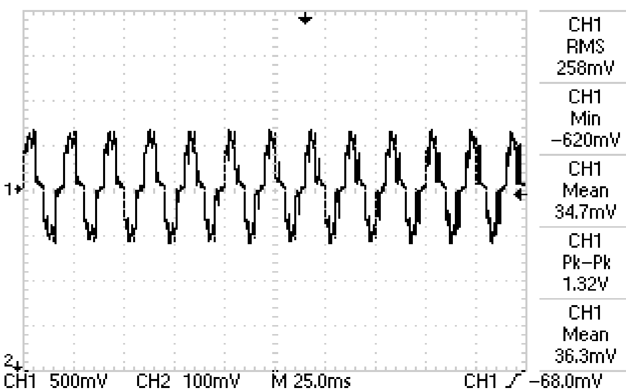

Figure. 5 (c). Electrical signal from the S3 membrane.

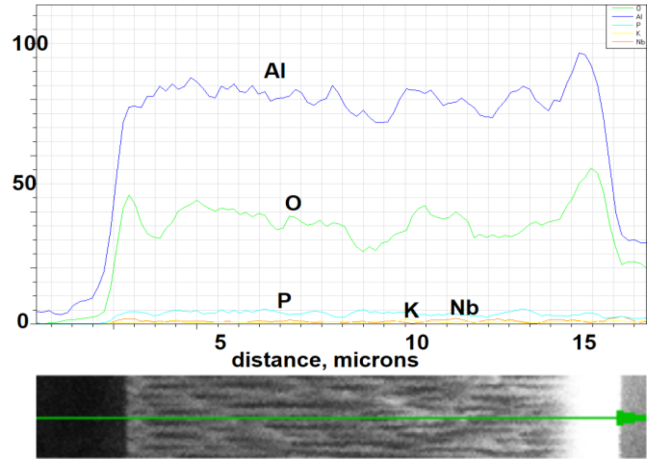

Fig. 6 (b). Elemental analysis of the membrane on S4 substrate.

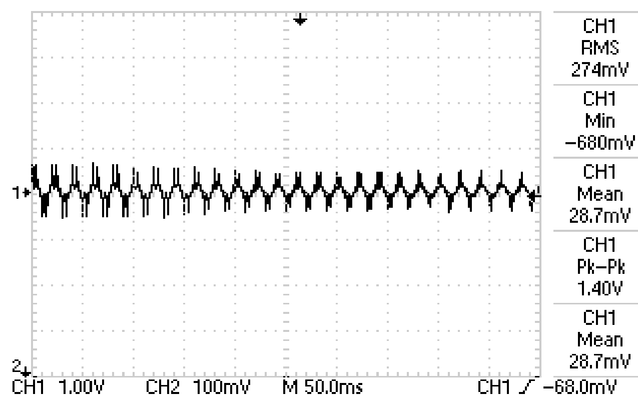

Fig. 6 (c). Electrical signal from the S4 membrane.

Deposition parameters on substrate S4:

AAO membrane fabricated by:

- one-step anodization at 100V and 13°C for 10 min; protect anode contact area of the substrate with photoresist to prevent undercut;
- final anodization at 150V and 13°C for 120 min;
- opening of pores bottoms with etcher CrO_3 +H_3PO_4;
- pores diameter expansion with CrO_3 +H_3PO_4 at 60°C for 30s.

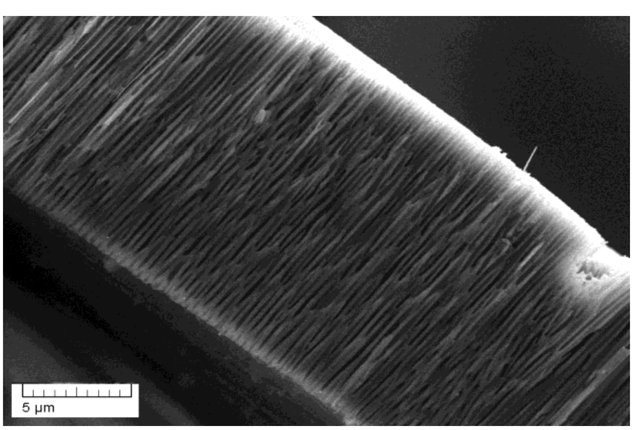

Fig. 6 (a). SEM image of AAO S4 membrane is observed penetration of piezoelectric material in pores volume (cross-sectional view) - **S4 Deposition**.

In our previous research [**17**] it was established that a flexible substrate with a functional area of 6 cm^2 and non-structured film of $KNbO_3$ with a thickness of 360 nm, achieved a maximum voltage of 480 mV. The highest generated voltage was 454 mV, generated from a membrane with a functional surface of 2.6 cm2 (structured and non-structured surface). This proves that the material is nanostructured and AAO can be used as a template for piezoelectric materials, but there is a need for additional optimizations. Future work will be related to the study of AAO membranes with a variety of geometrical parameters (pore diameter, thickness, etc.). To obtain better penetration in pores, there is a possibility to use piezo inks and piezo solutions.

Conclusion

The research in this paper shows the possibility for application of AAO as a self-structured nano-porous template for piezoelectric materials deposed by conventional microfabrication technologies. A good perspective for optimizing energy harvesting devices in terms of voltage increase was studied. The elemental analysis showed that on widened pores, there were uncoated zones of piezoelectric material. On the other side, membranes with reanodized pores show continuously presence of piezoelectric material along the pore wall. The obtained electrical signals proved that there was an electrical connection with the piezoelectric material from the two ends of the pores. From this data it can be concluded, that reanodized pores have a higher content of piezoelectric material without interruptions, as well as better density of deposition. Pores with expanded diameters show saturation in upper layers of AAO membranes, but inner volume deposition was not homogenous.

As a future work, it is envisaged to further study the effect of the pore diameter as well as the thickness of the oxide layer on the homogenous porous filing and the corresponding piezoelectric effect.

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Conflicts of interest
The authors have no competing interests to declare

Supporting information

There are no supporting informations at journal website.

Keywords

Piezoelectric nanostructures, Nanogenerators, Energy harvesting, Template-assisted growth, Porous aluminium oxide.

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Authors biography

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Graphical abstract

Our work is focused on structuring of piezoelectric material to achieve higher piezoelectric output signal. This is possible due to a porous matrix of anodic aluminum oxide used as a template. The main goal is to increase mechanical stress by nanowiring of piezoelectric material. Each structured nanowire serves as a stress concentrator of the external mechanical load. This is the reason to obtain higher output voltage compared to the same type and quantity of the non-structured material.