Development of topologically structured membranes of aluminum oxide

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Abstract. In recent years, nanomembranes have become one of the most widely used construction material for ultrasensitive and ultrathin applications in micro-electromechanical systems (MEMS) and other sensor structures due to their remarkable mechanical properties. Among these, the mechanical stability is of particular importance. We present an approach to the analysis of the stability of nanostructured anodic aluminum oxide free membranes subjected to mechanical bending. The membranes tested were with a thickness of 500 nm to 15 μm in various topological shapes; we describe the technological schemes of their preparation. Bends were applied to membranes prepared by using a selective process of etching and anodizing. The results of the preparation of the membranes are discussed, together with the influence of the angle of deflection, and the number of bendings. The results obtained can be used in designing MEMS structures and sensors which use nanostructured anodic aluminum oxide.

1. Introduction

The progress in micro- and nanotechnology stimulates the development of products with unique properties applicable in engineering, medicine, scientific research and everyday life. Some of them are employed to create a variety of sensors and micro- and nano-electromechanical devices. The predominant part of these devices use components made of membranes or beams [1]. Membranes are used in some gas sensors [2] and LED modules [3], and beams, in, e.g., acceleration sensors [4] or resonant sensors [5]. These structures are implemented as building blocks because they are easy to model, design and manufacture. Figure 1 presents schematically the different types of mechanical constructions used in the MEMS technology.

Membrane on a base

Membrane with a load

Beam with a load

Figure 1. Mechanical constructions.

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The aluminum base (1) is anodized and thus covered with an anodic oxide (2); this is followed by a selective etching of the aluminum oxide surface (3). Depending on the application, the mechanical constructions can be with (4), or without a load. In sensors of acceleration (accelerometers), for example, the load can be the mass of the oxide. The load can also be an area of metal or an additional element, such as an absorber of molecules and gases, a piezo element if constructing a pump, etc. Typically, the anodic aluminum oxide consists of a close-packed hexagonal array of nanopores [6]. During the anodization, the main parameters of the electrolytic process can be varied, which allows a precise control of the layer thickness, the pore size and the associated electrical and optical properties [7].

A significant advantage of the process of aluminum anodizing is that it can be easily combined with the planar technology used in microelectronics. Some of the sensors, and some MEMS devices as well, use membranes based on aluminum and its oxide, which is heated or subjected to mechanical stress. A good example is a gas sensor implemented on a membrane, with the membrane being heated to obtain the sensitivity needed [8]. This requires knowledge of the mechanical properties of the oxide and a long-term stability analysis of the membrane’s deformation (fatigue). Of particular interest are membranes or beams of small thickness. Examination of these elements requires the construction of appropriate test samples and the application of appropriate methods of examination.

2. Technological schemes for preparation of membranes
Two-sided photolithographic processing is used to implement topologically-structured membranes. Membranes with thicknesses of 400 nm – 500 nm to tens of microns can thus be prepared. Figure 2 illustrates the main processes involved in the preparation of a monolithic membrane with a certain topology.

![Figure 2. Technological scheme of membrane preparation.](image)

The preparation of a complete continuous membrane begins by laminating an aluminum foil (1) with a dry negative photoresist (2), which provides the necessary resolution and adhesion to the aluminum substrate. Using a photoresist, the precise dimensions in the implementation of the various configurations are defined. Before the exposure, the template (3) is aligned with the aluminum base using additional fiducial marks. The exposure of both sides is conducted through the protective foil for two minutes. The photoresist is developed only on one of the membrane’s sides (4), the other side of the sample being exposed (5) without developing in order to preserve the protective sheet. Then, anodic oxide (6) of different thicknesses is grown in the hole developed in the photoresist. Subsequently, the second side of the sample is developed using a spray developing technique, which is followed by etching off the aluminum in the resulting opening in the second side (7). The etching is performed by a selective etcher reacting with the aluminum, but not dissolving the oxide. The resulting anodic oxide layer (8) forms a beam or a membrane depending on the topology.

3. Experimental results
The technological experiments were carried out using a free strip of aluminum with a 99% purity. To reach the exact dimensions of the various configurations of the samples, we used a dry negative photoresist manufactured by Shipley Laminar GA (General Applications), with a thickness of 37 μm [9] and intended for for alkaline etching and acid electrochemical systems. This photoresist is
characterized by high performance, good resolution (50 μm) and high repeatability. The dry negative photoresist was applied by hot rubberized rollers using an Ozatek laminator. The selected mode of laminating was as follows: temperature of the rollers of 100 ± 10 °C, speed of motion of the rollers 0,4 – 1,5 m/min, air pressure 2 – 4 bar. After lamination, as recommended by the manufacturer, the layer was left to homogenize for a minimum of 15 minutes before any further technological process was initiated. The exposure was carried out by UV light through a mask (Figure 3) at intensities 55 mJ/cm² to 95 mJ/cm². The exposure time on both sides of the template was two minutes. The photoresist on the first side of the test specimen was developed in a 1-% solution of sodium carbonate (Na₂CO₃) containing 1 ml to 1,5 ml defoamers at 30 ± 2 °C for three minutes. The process was controlled visually by illuminating by a selective light. The second side of the sample was not developed in order to preserve the protective sheet. In the opening developed in the photoresist, anodic oxide was grown with thicknesses ranging from 0.5 μm to 15 μm. The oxide layers were produced in electrolyte of 5 % oxalic acid at a temperature of 15 °C and a potential of 4,0 V. The oxide layer formed in 10 minutes was dissolved selectively in a solution of phosphoric and chromic acid to obtain regular nanosized grooves. When re-anodizing an aluminum surface prepared in the way described, a cell structure is grown with a high degree of order. Under the specified conditions of the electrolysis process, the growth rate of the oxide was 0.1 μm/min and the average pore diameter, about 30 nm.

To create different configurations of membranes and beams, structures were used produced in one production cycle. Figure 3a presents the test photomask used in the experiment, where 1 is the topology of the oxide, 2 is the topology of the opposite etching, and 3 is a fiducial mark. Figure 3b shows samples of slugs with different oxide thickness for test beams.

Once the anodic aluminum oxide was grown, the second side of the test specimen was developed using a spray development technique and the aluminum in the resulting opening was etched off. The etching was performed by a selective etcher that reacts with aluminum but does not dissolve the oxide. Figure 4 illustrates the second stage of etching the back side of the test specimen.

Experiments showed that the process of photoresist removal from the front side and the simultaneous etching of both sides of the free aluminum surface is uncontrollable due to the exothermic reaction and the considerable deformation of the oxide. This is why we chose the one-side etching (from the bottom side). Figure 5 shows a stage in the samples preparation, where: 1 – aluminum is etched and a (transparent) oxide beam is formed; 2– meniscus of solution not wetting
the photoresist, 3 – photoresist (free) under which the aluminum is etched; 4 – oxide layer under which the metal has not been removed yet; 5 – photoresist under which the metal has been removed. A detailed fragment of the process, observed under a microscope, is shown in figure 6. A MIK 4 microscope was used at a magnification of 150 and side lighting.

The resulting detailed fragment of the process is formed by: 1 – oxide with etched metal; 2 – residue from the process of aluminum etching; 3 – photoresist without metal underneath; 4 – photoresist with aluminum underneath; 5 – oxide with aluminum underneath.

One of the major problems encountered in implementing this scheme was to prepare free thin films with thicknesses of less than 4 μm. As a result of the wetting of the oxide and of its thermal response under its own weight, a substantial number of the beams were braking in their base. To avoid this problem, we developed a new series of test items containing different configurations of beams and membranes. Figure 7 shows the resulting elements, where: 1 – a channel for separation of groups of samples; 2 – a comb of membranes; 3 – a free membrane held by the photoresist; 4 – residue of the etcher; 5 – a broken beam.

Of particular interest was to study the membranes retention by the resulting support frame of dry photoresist. We found that the anodizing and the concurring processes result in lifting the photoresist (1) while below it another anodizing process takes place where a gradual thinning is performed (3) (figure 8). This tucked oxide (2) with thickness over 4μm is sufficient to support the membrane, depending on its mass.

![Figure 7. Resulting elements.](image1)

![Figure 8. Membrane holding.](image2)

Figure 9 shows various kinds of beams glued to holders, which were developed specifically for the purposes of the experiment. Each beam is checked prior to testing for the presence of cracks (figure 10): 1 – photoresist; 2 – oxide on aluminum; 3 – a beam of oxide; 4 – a crack. Evaluation of the mechanical stability of free membranes of nanostructured anodic aluminum oxide can be carried out by measuring the deflection of the test sample at different loads.

![Figure 9. Beams.](image3)

![Figure 10. Cracks.](image4)
Figure 11 illustrates the experimental setup for mechanical impact studies. Initial experiments of measuring the load were conducted by lowering the needle attached to the analytical scale which measures a change of the weight of 0.1 milligram (1 – aluminum base level; 2 – direction of the oxide beam – 8 μm). In this case, the load caused by lowering the needle leads to bending of the beam at an angle of $\alpha = 15.7^\circ$ (for a total load of 701.3 mg) and $\beta = 19.2^\circ$ until impact at the base. The overall weight of the sample and the holder was 683.1 mg.

Detailed studies with various loads, thicknesses and directions of bending will be the subject of a future work.

![Experimental setup](image)

**Figure 11.** Experimental setup.

4. Conclusions

In recent years, nanomembranes have become one of the most widely used major structural components in the production of various types of nanoscale sensors, optical and micromechanical devices. Based on literature data, we developed a methodology for preparation of topologically-structured membranes of aluminum oxide. The main techniques used were electrochemical anodizing, photolithography and selective etching of aluminum. Using the technological scheme developed, we were able to fabricate membranes with a wide range of thicknesses and topological structures. The resulting oxide elements can be used in various applications in the micro and nanoelectronics.

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