Mechanical stability of heat-treated nanoporous anodic alumina subjected to repetitive mechanical deformation

A Bankova$^{1,3}$, V Videkov$^1$, B Tzaneva$^1$ and M Mitov$^2$

$^1$Technical University of Sofia, 8 Kliment Ohridski Bldv., 1000 Sofia, Bulgaria
$^2$Visteon Electronics Bulgaria Ltd., Capital Fort Building, 90 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria

E-mail: a_bankova@tu-sofia.bg

Abstract. We report studies on the mechanical response and deformation behavior of heat-treated nanoporous anodic alumina using a micro-balance test and experimental test equipment especially designed for this purpose. AAO samples were characterized mechanically by a three-point bending test using a micro-analytical balance. The deformation behavior was studied by repetitive mechanical bending of the AAO membranes using an electronically controlled system. The nanoporous AAO structures were prepared electrochemically from Al sheet substrates using a two-step anodizing technique in oxalic acid followed by heat treatment at 700 °C in air. The morphological study of the aluminum oxide layer after the mechanical tests and mechanical deformation was conducted using scanning electron and optical microscopy, respectively. The experimental results showed that the techniques proposed are simple and accurate; they could, therefore, be combined to constitute a method for mechanical stability assessment of nanostructured AAO films, which are important structural components in the design of MEMS devices and sensors.

1. Introduction

The mechanical stability and durability of thin oxide films is a major concern in the operation and reliability of microelectromechanical systems (MEMS). Numerous articles and reports have appeared dealing with the characterization of the mechanical properties of polysilicon [1-3]. Nowadays, anodic aluminum oxide (AAO) is also being used in MEMS as a structural material, especially in the fabrication of AAO membranes for pressure or microheaters-based sensors [4-6]. As the thin films are exposed to adverse environments, which makes the oxide layer expand or stretch, the mechanical behavior plays a significant role in their usage in MEMS technology. Therefore, the ability becomes essential of determining the mechanical stability and fracture behavior of porous alumina films, in view of designing reliable layers in MEMS sensors and devices. Most studies on the mechanical properties of AAO films have been focused on using the nano-indentation and microhardness tests [7-9]. However, these methods have to do with measuring the parameters on a micro- and nano-scale and require expensive and complex equipment. Furthermore, few publications have appeared dealing with studies on the mechanical stability of anodized aluminum.

$^3$To whom any correspondence should be addressed.
The aim of this work was to assess the mechanical behavior of nanostructured heat-treated AAO membranes using two measurement techniques. The first one is the well-known three-point bending test, which was performed on a special micro-analytical balance. This technique can also be used to measure the deflection to failure of the anodic aluminum oxide. The second one is based on specially developed experimental setup for repetitive mechanical bending of nanostructured membranes of aluminum oxide, i.e. characterization of the stress in oxide layers of small thickness. The experimental results from this test are used to determine the mechanical properties of the oxide, such as fatigue and cycles to fracture (breaking) of the material.

2. Specimen preparation

2.1. Fabrication of AAO membranes

Nanoporous AAO was prepared electrochemically using a two-step anodization technique in an oxalic acid solution. Specimens for the bending test were fabricated by anodizing free strips of aluminum foil with a 100-µm thickness and 99% purity. Part of the aluminum sheets were annealed at 220 °C in air for 30 min to release the mechanical stresses and were then electro-polished for 45 s in a solution of 200 mL orthophosphoric acid at a current density of ~3A/cm², in order to improve the surface quality of the substrate. After electropolishing, the test samples were washed with deionized water. The anodization process was carried out in oxalic acid in a voltastatic mode. The detailed experimental conditions of the electrolysis process whereby oxide layers were grown are summarized in table 1.

| Electrolyte    | Temperature (°C) | Potential (V) | Duration (min) | Diameter of pores (nm) | Thickness of layers (µm) |
|----------------|------------------|---------------|---------------|------------------------|------------------------|
| Oxalic Acid    | 15               | 40            | 60            | 30                     | 6                      |

Separation of the resulting oxide from the aluminum substrate was performed by liquid chemical etching of the aluminum. Details on the anodization steps are described in [10]. The surface morphology of the specimens was investigated by scanning electron microscopy (SEM). The SEM micrographs presented in figure 1 show a well-defined, self-ordered, nanoporous AAO structure. The geometrical dimensions of all AAO film were 7 mm in length and 5 mm in width.

Figure 1. SEM image of the AAO surface morphology viewed from the porous layer side (a) and from the bottom layer side (b).
2.2. Heat treatment
The main focus of this work was determining the mechanical response and deformation behavior of heat-treated nanoporous anodic alumina oxide. Recently, the polymorphic phase transformations in AAO structure have been of interest to those intending to use AAO membranes in applications requiring mechanical strength. Thus, further research is needed to understand thoroughly the mechanical properties of AAO films. After the anodization process, part of the AAO samples were heat-treated at 700°C for four hours, in order to compare the mechanical response of heat-treated and non-heat-treated AAO membranes. The heat treatment was performed in air in a high-temperature furnace. To prevent thermal cracking of the oxide material, the extremely low heating rate of 10 °C/min was chosen. The temperature of the tube furnace was controlled by a digital temperature controller with an accuracy of ±1 °C. The thermal profile of the furnace is shown on figure 2. The structures of the experimental samples prepared were characterized by means of optical monitoring.

All specimens numbered from N1 to N4 were prepared under the same anodization conditions with a thickness of 6 μm, which was measured using optical microscopy. The specimens used for the experiment are described in table 2.

3. Testing methods and discussions
In order to describe and mechanically characterize the heat-treated nanoporous AAO films, the following tests were carried out:

3.1. Three point bending test
The mechanical response of the AAO specimens prepared was measured by a three-point bending test at room temperature. An analytical balance with an accuracy of 0.1 mg was used to record the force applied to the sample. We should note that measuring the deflection of a membrane versus the applied force using an analytical balance avoids the error due to the force vector decomposition. A schematic diagram of the experimental setup for the three-point bend test is shown in figure 3.

The principle of the method presented in this paper is based on the following procedures: The experimental sample (1) is laid horizontally over two supporting thin plates (2), which are fixed at one end to a carrier (3). The force is applied to the top of the material through the blade (7), which is attached to a holder (8). The blade is moved to the support of the nanomembrane (1) by a micrometric screw through the console (9), which is connected to the holder (8). The experimental specimen, together with the carrier (3), are placed on a plate balancing system, which is made of a plate (4), bearing strings (5) and a rocker arm (6). This is done in order to achieve horizontality of the two supporters and parallelism of the blade relative to the specimen. Using the setup described, one obtains the dependence of the membrane deflection on the force applied. In addition, this experimental setup can be used to measure the Young’s modulus of a beam-shaped sample, which will be the subject of a future work. Figure 4 present a photograph of the bending deflection of a beam with a 6-μm thick heat-treated oxide, where the load/deflection ratio is 2.45 mN/352 μm.

In all measurements, the distance between the two supports in the three-point bending test was 5 mm and the load was applied in the middle between them. Depending on which side of the experimental sample the load is applied (the porous side or the bottom barrier side), the membrane...
will have different bending behavior. In the three-point bending test, the surface of the nanoporous oxide in contact with the loading blade will be subjected to a compressive stress and the other surface touching the two supporting beams, to a tensile stress. In this study, the load was applied only to the porous side. Table 3 summarizes the relationship between the bending deflection and the applied load at 300 μm and 500 μm blade displacement in relation to the supporting plates.

![Figure 3. Schematic diagram of the three-point bending setup.](image1)

![Figure 4. Deflection determination (measuring) using an optical microscopy image.](image2)

**Table 3. Experimental results of three-point banding test.**

| Sample | 300 μm | 500 μm |
|--------|--------|--------|
|        | Load (mN) | Deflection (μm) | Load (mN) | Deflection (μm) | Fracture |
| N1     | 2.13     | 0       | 2.62     | 430           | No       |
| N2     | 2.12     | 56      | 2.31     | 307           | No       |
| N3     | 2.12     | 0       | 2.41     | 436           | No       |
| N4     | 2.13     | 0       | 2.81     | 377           | No       |

As one can see, the deflection of the non-heat-treated oxide (samples N1 and N3) is slightly higher than that of the heat-treated oxide (samples N2 and N4). This is due to the difference in the morphology and crystalline characteristics between the anodized oxide and the oxide subjected to heat-treatment. During the experimental tests, no fracture occurred in the oxide samples, although the deflection of the specimen exceeded the thickness of the AAO film by a factor of 1000. Furthermore, a slide of the specimen at the two supports was observed using a digital microscope. The cause of the slide is the bending deflection of the specimen resulting from the load applied. When the applied force was removed, the AAO specimen was recovering rapidly from the state of deflection. This indicated that the deformation of the specimen was still within the elastic range (figure 5).

### 3.2. Repetitive bending test

In order to evaluate the mechanical stability of the test specimens, they were subjected to mechanical deformation (bending). A specially designed test equipment (figure 6) was developed to provide repetitive bending. It consisted of a stepper motor (1) coupled to a camming mechanism (2, 3, 4), which pushes a steel rod (7). A soft-steel spring (5) pushes the rod back to the camming mechanism in order to prevent mechanical jittering. The rod moves through a bronze sleeve (6) to minimize the
friction between the rod and the sleeve. The specimen is mounted on an aluminum carrier (8) above the rod. When the shaft of the stepper motor rotates, it drives the camming mechanism which pushes the rod forward when it is going up. When the camming mechanism is going down the rod goes down too because the spring pushes it back. The forehead of the rod is polished and is in contact with the AAO specimen (9). The specimen thus follows the movement of the rod. We were able to control the bending angle of the nanostructured AAO films with the use of microcontroller system driving the stepper motor. The maximum frequency of the repetitive bending was 2.5 Hz. Figure 7 is a photograph of the system.

Each membrane was bent to an angle of ~40° (figure 7) one million times. After the test, all the specimens were examined by optical microscopy. No cracks or defects were observed. The accuracy of the programmable system designed for repetitive mechanical bending of nanostructured oxide membranes is achieved through the precision of manufacturing of its mechanical components.

5. Conclusions
The mechanical response and deformation behavior of nanoporous alumina films were studied. AAO films with 6-μm thickness were produced by a two-step anodization process in an oxalic acid solution. The heat treatment of the AAO films tested had significant effects on their mechanical response. Additionally, no obvious differences in the four types of experimental samples appeared as a result of repetitive bending tests.
References

[1] Cambie R, Carli F and Combi C 2003 Proc. Int. Conf. on Microelectronic Test Structures (2003 Monterey CA USA) pp 3-39
[2] Tabata O and Tsuchiya T 2008 Reliability of MEMS: Testing of Materials and Devices (Weinheim, Germany: John Wiley & Son)
[3] Pasquale G and Somà A 2010 Sensors 10 456
[4] Park S, Lee D, Byun S, Yoo H, Park D, Hwang W and Choi J 2016 Int. J. Electrochem. Sci. 11 7401
[5] Routkevitch D, Polyakov O, Deininger D and Kostelecky C 2005 NSTI-Nanotechnol. 2 266
[6] Chen W, Gui X, Liang B, Yang R, Zheng Y, Zhao C, Li X, Zhu H and Tang Z 2017 ACS Appl. Mater. Interfaces 9/28 24111
[7] Hu Z, Shrestha M and Fan Q 2016 Thin Solid Films 598 131
[8] Fang T, Wang T, Liu C, Ji L and Kang S 2007 Nanoscale Res. Lett. 2/8 410
[9] Ko S H, Lee D W, Jee S E, Park H C, Lee K H and Hwang W 2005 Glass Phys. and Chem. 31/3 356
[10] Bankova A, Videkov V and Tzaneva 2014 J. Phys.: Conf. Ser.ies 514 012027