Nanoindentation study of the mechanical properties and deformation behavior of nanoporous alumina films

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Abstract. Over the past decade, anodic aluminium oxide (AAO) has become one of the most widely used materials as a platform for developing new types of devices in micro- and nanotechnology. Due to the potential use of highly ordered honeycomb porous AAO membranes in many engineering applications, considerable attention is being paid to the mechanical characterization of such thin films. In this study, the mechanical properties and deformation behavior of a nanoporous alumina film were investigated by nanoindentation. AAO films with an average pore diameter of 40 nm were fabricated electrochemically. The morphology and the mechanical properties of AAO were studied using scanning electron microscopy and nanoindentation, respectively. The force-displacement dependences obtained revealed that in the case of a freestanding AAO membrane the sample demonstrates extremely high elasticity. The indentation modulus and the hardness were found to decrease nonlinearly with an increase in the applied force.

1. Introduction

The research and development of nanoporous templates have rapidly progressed over the last two decades due to their relative simplicity and applicability to industrial scale production [1, 2]. Porous membranes, such as anodized metal oxides, have been employed in a variety of engineering applications. Anodic aluminium oxide (AAO) is among the most extensively used oxides. Nano-honeycomb structures, such as AAO films, have a combination of properties, including high hardness, high thermal stability and high corrosion resistance [3, 4]. Thanks to these properties, AAO membranes can be applied as substrates in the fabrication of complex microstructures for micro-electromechanical system (MEMS) devices [5, 6]. Anodized aluminium has also found application in enclosing and packaging of devices, such as MEMS RH sensors [7] and MEMS DC response accelerometers [8], microfluidic devices, etc. [9-12]. Mechanical stability and durability are prime requirements to the thin AAO films in view of production of reliable electronic devices incorporating...
AAO. Therefore, it is important to know the mechanical properties and deformation behavior of the porous alumina film.

Numerous studies have used various methods to evaluate and measure the mechanical properties of AAO [13-15]; one of the easiest ways to assess small-size specimens is by using a bending test [16, 17]. In our work, the bending tests were carried out by a nanoindentation technique based on an atomic force microscope (AFM) equipped with a calibrated diamond Berkovich tip. The indenter tip has a direct impact on the AAO membrane by pressing the sample surface normally by a controlled force. Bending tests were performed on both sides of the nanostructured AAO film. The information obtained through the nanoindentation measurements is a load-deflection curve, which allows one to determine experimentally the elastic modulus and the hardness of the nano-honeycomb AAO films. The experimental results revealed a relationship between the direction of the mechanical impact and the AAO pores’ vertical direction. The results of this study could be useful in understanding the mechanical stability and deformation behavior of nanoporous alumina films.

2. Experimental part

2.1. Fabrication of AAO membranes

Three types of AAO membranes were prepared in order to determine the dependence of the mechanical properties on the deformation force applied during the AFM bending test. Well-ordered porous-type AAO films were fabricated by electrochemical anodization technique with thicknesses ($h$) of 1 μm and 4 μm. A strip of aluminium foil with a 100-μm thickness and 99% purity was used as a substrate material. After a standard substrate cleaning, the aluminium sheet was anodized in 4 wt % oxalic acid solution under a potential of 40 V at 15 °C. The morphology and structure of the porous oxide membranes prepared were observed by a scanning electron microscope (SEM) – the specimens had a pore diameter ($d$) of 40 nm and inter-pore distance ($D$) of 110 nm. The thickness of the barrier layer ($z$) was approximately 42 nm. Table 1 presents a description of the samples and the structural features of the nano-honeycomb structures obtained:

| Sample No. | Sample Description                  | $h$ [$\mu$m] | $d$ [nm] | $z$ [nm] | $D$ [nm] |
|------------|------------------------------------|--------------|-----------|-----------|----------|
| N1         | AAO membrane                       | 4            | 40        | 42        | 110      |
| N2         | AAO membrane with Ni-filed nanopores | 4            | 40        | 42        | 110      |
| N3         | Freestanding AAO membrane          | 1            | 40        | 42        | 110      |

The first sample (N1) was a nanoporous AAO membrane with a 4-μm thickness and a removed aluminium substrate. The resulting oxide was separated from the aluminium layer by wet chemical etching of the aluminium. Details on the anodization steps are summarized in [18]. In order to understand better the mechanical deformation behavior of the AAO films, another sample (N2) was fabricated. As a starting material we used a nanostructured membrane sample (N1), where the AAO through-channels were filled with nickel by electrochemical deposition. The fabrication process steps and conditions of the electrochemical metal deposition technique were reported in [19]. Electrodeposited nickel films having high strength and corrosion resistance are often used in manufacturing MEMS components.

A third sample (N3) was fabricated by a UV lithographic process producing a freestanding membrane with a circular shape, as shown in figure 1. To form circular patterns, a negative photoresist on the AAO membrane was exposed to UV. The aluminium layer was removed by etching. The freestanding AAO membrane thus prepared had a thickness of 1 μm and a diameter of 4.5 mm. The
fabrication procedure is described in detail in [18]. All samples were examined by optical microscopy before and after every bending test. No cracks or defects were observed.

2.2. Bending sample testing
A compact bending test with an AFM-based nanoindentation technique was performed to measure the hardness and elastic modulus of the produced nanostructured AAO films. Figure 2 shows a SEM image of a cross-section of the AAO freestanding membrane with well-ordered nanopores.

The nanoindentation measurements were carried out using a Triboscope Nano-Indenter (Hysitron Inc), equipped with a Berkovich indenter with a 240-nm tip radius. The indenter head was used to apply force in the vertical directions of the sample without leaving an imprint pattern on the surface of the AAO film. Figure 3 shows the setup for bending the samples tests. Samples N1 and N2 with their entire length were mounted on a stainless steel support using carbon tape; sample N3 was fixed at both ends.

The top surface of a sample in contact with Berkovich tip is under a compressive stress, whereas the bottom surface is subjected to tensile stress. The nanoindentation experiments revealed a significant difference in the mechanical behavior of the AAO material depending on the side of applying the bending force, as clearly demonstrated by the load-displacement curves of the freestanding membrane.

Considering the anisotropic properties and mechanical nature of AAO honeycomb structures, the barrier layer of the AAO membrane would resist a higher tensile stress than the porous side. Additionally, the influence of the pore structure, particularly the uniform filling of pores by electrochemical deposition, will affect the deformation mechanisms of porous AAO. This is confirmed by the experimental results obtained by the AFM nanoindentation measurements presented and discussed in the next section.
3. Results and discussion
In the AFM bending tests, the indentation load was applied by a Berkovich tip within the loading range from 400 μN to 3000 μN without leaving an imprint pattern of deformation on the AAO material. The tests were carried out on both sides of the AAO specimens (porous and barrier layer) in at least five different regions of the sample surface, thus exploring the variation of the load-displacement behavior at different loading points in search of a better understanding of the anodic aluminium oxide’s mechanical properties.

The vertical position of the tip and the vertical displacement of the experimental samples were recorded and converted to load–deflection curves, the latter allowing us to determine the mechanical properties and deformation behavior of the porous AAO membrane. Figure 4a shows the load-displacement curves depending on the different loading rates applied to sample N1. As seen, the hysteresis width between the loading and unloading curves increases with the increase of the applied loading force. This characterizes the relative elastic behavior of the AAO membrane during the indentation measurement. For an applied force of 3000 μN (figure 4b), the mechanical properties of the AAO material depend strongly on the direction of applying the load in relation to the orientation of the pores, namely, a greater elastic deformation is registered when the barrier layer is under loading. This capability of resisting compressive stress is a typical feature of most ceramic materials [20]. The width of the hysteresis loops of the two load-deflection curves is similar, showing analogous response to deformation.

![Figure 4](image_url)

**Figure 4.** Load-displacement curves of AAO membrane N1 at (a) 400, 2000 and 3000 μN loading rates and (b) 3000 μN load applied on the porous and barrier layer sides

The elastic modulus and hardness of AAO specimen N1 were examined using the nanoindenter’s software. The results are summarized in table 2 and illustrated graphically in figure 5 and demonstrate a nonlinear decrease in the elastic modulus and hardness with an increase in the applied force, which is typical of a rounded Berkovich indenter tip.

| Nanoindentation | Load [μN] | Elastic Modulus [GPa] | Hardness [GPa] |
|-----------------|-----------|-----------------------|---------------|
| Porous Side     | 400       | 11.2                  | 33.35         |
|                 | 2000      | 2.8                   | 0.84          |
|                 | 3000      | 1.5                   | 0.44          |
| Barrier Layer   | 3000      | 1.0                   | 0.31          |

Table 2. Elastic modulus and hardness of N1 sample.
The dependence of the elastic modulus is described in terms of a polynomial function:

\[ E = 14.5 - 8.9 \times 10^{-3} F + 1.52 \times 10^{-6} F^2, \]  

(1)

where \( E \) is the elastic modulus [GPa], and \( F \), the applied load [\( \mu \)N].

Figure 5. Dependence of the elastic modulus and the hardness on the applied force.

Figure 6. Load-displacement curves at 3000 \( \mu \)N of AAO samples N1 and N2.

Figure 6 illustrates the indentation load-displacement curves obtained for specimens N1 and N2 at the same loading rate. The deformation mechanism of porous anodic aluminium oxide is strongly dependent on the structure, particularly on whether the pores are filled or not [21]. As seen in figure 6, the electrodeposited nickel sample has a lower elastic modulus compared with sample N1. It is also seen that the hysteresis loop of the alumina+Ni sample is wider than the one of alumina only. The difference between the hysteresis loop widths under 3000 \( \mu \)N is due to the increased density and lower porosity in the Ni samples.

The load vs displacement curve of the freestanding membrane (sample N3) with 1-\( \mu \)m thickness is plotted in figure 7. In order to perform a better mechanical characterization of the thin AAO membrane, the load was applied on both sides of the sample at several different points. The load-displacement data obtained shows that the modulus of elasticity is greater in the barrier layer than in the porous layer. This is due to the barrier layer having a greater ability to resist to tensile stress compared to the porous side [21].

Figure 7. Load-displacement curves of sample N3 at 400-\( \mu \)N load applied at the a). porous side and b). barrier layer.
To explain the effect observed, we present in figure 8 a schematic diagram of a deformed porous membrane under tensile stress. Considering the dense structure of the barrier layer of the AAO film, the "resistance effect" becomes visible. Another important conclusion to be drawn from the results in figure 7 is that the mechanical behavior of nanostructured materials and the deformation mechanisms depend also on the point of loading. When the force is applied along the periphery of the AAO sample, a higher modulus of elasticity is observed compared to the bending force being applied to the center of sample N3. Also, the load-displacement curves in figure 7 do not exhibit a hysteresis loop, indicating a completely elastic deformation response.

4. Conclusions
The mechanical properties and deformation behavior of nanoporous alumina films were investigated by an AFM nanoindentation technique. Three types of AAO membranes were produced by electrochemical anodization in an oxalic acid solution. For better understanding the mechanical deformation of the material, the through-channels of one of the samples were filled with nickel by electrochemical deposition. The results from the bending test revealed that the alumina+Ni sample exhibited a lower modulus of elasticity and reduced deflection under load compared to the pure alumina membrane. Force-displacement curves obtained during nanoindentation experiments by a Berkovich tip were used to determine the hardness and elastic properties of the AAO specimens. The side of force application has significant effects on the mechanical behavior of alumina film. The barrier layer of the AAO film exhibited a better resistance to tensile stress and a higher elastic modulus compared to the porous side of the film.

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