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FABRICATION AND CHARACTERIZATION OF HIGHLY ORDERED NANOTUBES OF ANODIC ALUMINUM OXIDE

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Investigated the electrochemical synthesis and characterized of a nanometer scale porous anodic aluminum oxide (AAO) membrane with a mean pore diameter of about 80-100 nm. The anodizing process was done by varying the anodizing temperature from 20 °C to 25 °C. The membranes exhibit interesting properties such as controllable pore diameters, periodicity, and density distribution. These properties can be adjusted by controlling the parameters of a temperature-controlled two-step anodization process. The surface features of the nanometer scale membrane such as pore density, pore diameter, and interpor distance were quantified using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The SEM and AFM investigations revealed the presence of focal adhesion sites on the surface of the porous membranes. The positive outcomes of the study indicate that AAO membranes can be used for applications in the future.

Keywords: anodic aluminum oxide, two-step anodization, nanometer, nanopore, SEM, AFM, XRD

ИЗГОТОВЛЕНИЕ И ХАРАКТЕРИСТИКА ВЫСОКОУПОРЯДОЧЕННЫХ НАНОТРУБОК АНОДНОГО ОКСИДА АЛЮМИНИЯ

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Исследовали электрохимический синтез и определили характеристики мембран из пористого анодного оксида алюминия (AAO) на нанометровом масштабе со средним диаметром пор около 80-100 нм. Процесс анодирования осуществлялся путем изменений температуры анодирования от 20 °C до 25 °C. Мембраны продемонстрировали интересные свойства, такие как контролируемые диаметр пустот, периодичность и распределение плотности. Эти свойства можно предварительно выбрать, настраивая условия двухступенчатого процесса анодирования с контролируемой температурой. Характеристики поверхности мембран на нанометровом масштабе, такие как плотность пор, диаметр пор и межпористое расстояние, были определены с использованием сканирующей электронной микроскопии (SEM) и атомно-силовой микроскопии (AFM). Исследования SEM и AFM показали наличие очаговых участков адгезии на поверхности пористых мембран. Положительные результаты исследования показывают, что мембраны AAO могут быть использованы в будущем.

Ключевые слова: анодный оксид алюминия, двухступенчатое анодирование, нанометр, нанопоры, SEM, AFM, XRD

YUQORI DARAJADA TARTIBLASHGAN ANODLI ALUMINYY OKSIDI NANOGRUBLAR KALARIINI OLISH VA XARACTERLASH

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Исследовали электронную микроскопию (SEM) и атомно-силовую микроскопию (AFM). SEM и AFM исследования показали некоторое количество очаговых участков адгезии на поверхности пористых мембран. Положительные результаты исследования показывают, что мембраны AAO могут быть использованы в будущем.

Ключевые слова: анодный оксид алюминия, двухступенчатое анодирование, нанометр, нанопоры, SEM, AFM, XRD

Introduction

The anodization process of metals has been used by industry to protect metal components from corrosion for approximately 90 years. During this electrochemical process, the surface chemistry of the metal changed, via oxidation, to produce an anodic oxide layer that is thick enough to stifle further oxidation [1]. Aluminum, when is anodized, forms self-organized arrays of cylindrical pores, and this phenomenon was detected by Keller et al [2]. Masuda et al. in 1995 and Jessensky et al. in 1998 described the anodization process on Al foil with ordered hexagonally parallel nanotubes using a two-step anodization technique. The nanotubes are getting ordered form the bottom and up in the anodization process [3].

Anodization of aluminum, under certain conditions, can yield large aspect ratio nanopores with a pore diameter in the range of 10-200 nm and pore depth of several μm [4]. It was during the long anodization periods (up to a maximum of 160 hours) used throughout their studies that the pores were able to self-adjust from their random initiation sites. The ordered pore positions only seen at the metal/oxide interface after the barrier layer removed. The initial pore sites seen on the surface of the oxide/electrolyte interface were the result of the random nucleation sites produced during the early stages of oxide formation [9]. Aluminum anodization is one of the most controllable self-assembly processes, and nanoporous anodic aluminum oxide has em-

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employed to synthesize a variety of nanoparticles and nanowires through a template-mediated approach [5].

Mainly, the following chemical processes dominate the anodization of the alumina membranes [2].

(1) $\text{Al}^{3+}$ ions form at the metal/oxide interface and distribute in the oxide layer near the oxide/metal interface:

$$\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}.$$  \((1)\)

(2) The electrolysis of water occurs at the pore bottom near the electrolyte/oxide interface:

$$2\text{H}_2\text{O} \rightarrow 2\text{O}^{2-} + 4\text{H}^+.$$  \((2)\)

(3) Due to the electric field, the $\text{O}^{2-}$ ions migrate within the barrier layer from the electrolyte/oxide interface to the oxide/metal interface, and react with the $\text{Al}^{3+}$ ions there, forming $\text{Al}_2\text{O}_3$:

$$2\text{Al}^{3+} + 3\text{O}^{2-} \rightarrow \text{Al}_2\text{O}_3.$$  \((3)\)

(4) And there is an electric-field-enhanced oxide dissolution at the electrolyte/oxide interface:

$$\text{Al}_2\text{O}_3 + 6\text{H}^+ \rightarrow 2\text{AlF}_3(\text{aq}) + 3\text{H}_2\text{O}.$$  \((4)\)

Electrodeposition into nanoporous alumina has been used to fabricate metallic nanowires of nickel, silver, gold, cobalt, copper and palladium, among others. Nickel and cobalt nanowires used for applications such as, magnetic storage whereas palladium nanowires have been used as hydrogen gas sensors and electro catalysts in direct alcohol fuel cells and in biofuel cells [4, 6]. Thus, a new hypothesis has generated to explore the relationship between anodizing parameters and substrate properties on nanostructured AAO film in microstructural and chemical properties in order to enlarge its usage especially in electronic applications.

### Research methods

The nanoporous alumina templates where fabricated through a two-step anodization of polycrystalline aluminum films polished to a mirror finish. We used aluminum films (99.8%) from Sigma-Aldrich to prepare the porous aluminum oxide. Experiments carried out according to the scheme given in Fig. 1. In order to obtain well-ordered porous AAO with various pore diameters anodization in oxalic acid. After production of the samples, characterization of mechanical and wetting properties performed, including possibilities to electrodeposit Ni nanowires.

The most important step in the pretreatment of aluminum before anodizing is the polishing of the samples. For aluminum, this can be achieved by means of mechanical, chemical, or electrochemical polishing; in our case mechanical polishing used to prepare smooth Al surfaces before anodizing. During the first anodization, the pore structure on the surface badly arranged. By removing this non-regular oxide layer, a periodic concave pattern formed on the aluminum surface. Then the second anodization carried out at the same anodizing potential as that used for the first anodization, thus, forming well-ordered AAO surfaces. The anodization carried out in oxalic acid at voltage of 40 V.

The conditions of anodic oxidation depending on the selected electrolyte is given in Table 1.

**Results and discussion**

**Porous film growth.** The study of the process of anodic oxidation of aluminum showed that an ordered pore structure formed only under certain conditions. For example, aluminum oxide with a distance between pores equal to 50, 65, 100, 420, and 500 nm formed at a voltage of 19 and 25 Volts (V) in sulfuric acid, at 40 V in oxalic acid, at 160 and 195 V in phosphoric acid [6].

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<table>
<thead>
<tr>
<th>Oxidation steps</th>
<th>Electrolyte</th>
<th>Anodizing voltage and current, V; A</th>
<th>The duration of oxidation, hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>The first oxidation</td>
<td>0.1M (COOH)$_2$</td>
<td>40; 2</td>
<td>2</td>
</tr>
<tr>
<td>The second oxidation</td>
<td>0.1M (COOH)$_2$</td>
<td>40; 2</td>
<td>1</td>
</tr>
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Figure 1. Experiment flow chart.
It generally accepted that the porous structure of the anodic alumina film develops from the barrier-type coating formed on aluminum at the start of anodization. Growth of the barrier film occurs due to the high field ionic conduction and the constant filed strength, defined as a ratio of the potential drop across the barrier film to its thickness [2].

Anodization process takes place with the oxygen ions present in the electrolyte, which reacts with the surface of the Al to remove the $\text{Al}^{3+}$ ions. The motivation of this work is to lower the time taken for the anodization process and to analysis the AAO pore formation using oxalic acid. Time taken for the first and second anodization were 4 hours, respectively. In the context of fabricating AAO pores with diameter and wall thickness of $\sim100$ nm, two step anodization using oxalic acid was attempted. The initial step is to create a template for the oxide growth along with the pore formation. Oxalic acid anodization was carried out at a potential of 40 V, keeping the temperature constant at $\sim25^\circ \text{C}$. The higher anodic voltage and electrolyte concentration will make the oxide thickness larger because of the increasing of anodic reaction speed. This oxide thickness increase is mainly due to increasing of electrical current density with increasing of both electrolyte concentration and applied anodic voltage [7].

Alternatively, ordered, uniform-size pores have obtained in other work by patterning the initial aluminum film using a mold [8]. Pores at the upper part of the sample are straight, but distorted at the lower part. Microscopic undulations observed from the bottom side of the AAO, revealing plastic deformation of the aluminum substrate during anodization [10].

**Microstructural Characterization.** Figure 3 shows top view and 3-D view (AFM) of the aluminum film, and surface roughness of the aluminum was turned out to be quite good (average 126 nm). The average surface roughness value was derived from the cross-sectional analysis done by nanoscope image processing software. The analysis demonstrates evidence of porous alumina formation and reveals a multi-modal size distribution of pores for all the investigated samples. The best homogeneity of pores in both shape and order obtained for sample prepared.
Concerning the other anodization times, the pores lose their hexagonal ordering and become less consistent in shape. The average diameter of pores is found to be around 100 nm for sample A, respectively. AFM analysis indicates also an increase in pores average interval distance with anodization time.

We investigated the effects of sputtered aluminum on the morphology of anodized alumina using atomic force microscopy. The morphology of the anodized alumina strongly related to the original surface roughness of the as-sputtered aluminum. It suggests that ordered and stable anodic oxidation could not take place on the rough surface due to randomly oriented crystal directions of the as-sputtered aluminum. However, in this case, the thickness of the aluminum layer was too thin to undertake any full-scale electropolishing process. When we electropolished (the process which is described in the experimental section) the aluminum layer for a very short time, non-uniform tilted structural nanopores were formed, and the arrangements of pores were good.

The crystal structure of the aluminum alloy samples also analyzed using XRD. Figure 4 shows the X-ray diffraction pattern of aluminum and anodized aluminum samples. From the diffraction pattern, it noticed that the Al and Al₂O₃ phases are present in the anodized sample. This infers that after anodization, the porous Al₂O₃ layer formed on the substrate. X’pert high score plus (version 2.0) used to identify the peaks.

X-Ray diffraction studies by Fisch et al. found a mean interpore distance of around 0.37 nm for a typical anodic membrane [10]. The optimal voltage for ordering indicates the physics on the charge screening at the interface of the Al metal and the ion solution. For the positively charged Al surface, the negatively charge ions or anions in electrolyte can localized. The positively biased Al strongly attracts anions and provide electrons to form Al ions. The strongly interacting electrons at the metal surface contribute to form surface plasmon states and can diffracted to form the Friedel oscillation, causing the charge screening effect. The fluctuating surface charge density on the Al metal can redistribute by the electric field, so that the interval between nanoholes is proportional to the field. Therefore, according to the charge diffraction pattern of Al metal, the ordering of hexagonal nanohole array of AAO can be formed on the interface between Al metal and AAO layer.

**Conclusion**

In this work, porous and transparent alumina films with a well-ordered structure fabricated on a glass substrate. SEM and AFM used to characterize the structural and optical properties of the realized films. As demonstrated by AFM microscopy, a fine control of pore size and density achieved. It found that the pore diameter and interpore distance increases with increasing the anodization time. A strong correlation between microstructure and optical properties has demonstrated. High refractive index observed for films realized with high anodization time. Based on the two-step anodization process, oval-shaped pores were formed with about 80-100 nm pore diameter. XRD analysis showed the existence of Al₂O₃ peaks after anodization.
REFERENCES


