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Porosity and hole diameter tuning on nanoporous anodic aluminium oxide membranes by one-step anodization

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ABSTRACT

Nanoporous Aluminium (III) oxide was fabricated and characterized to determine its suitability as a microfiltration membrane and an antireflection coating. Aluminium (III) oxides were obtained using a one-step anodization process with Phosphoric acid (H_3PO_4) as electrolyte. The effect of the anodization voltage and electrolyte concentration were studied. Semi-ordered nanotubes were observed using a Scanning Electron Microscope. Porosity, pore diameter and interpore distance were obtained and were found to increase with an increase in anodization voltage. While the pore diameter and porosity increased with an increase in electrolyte concentration, the interpore distance was found to remain stable. The porosity was found to vary from 16% to 28% in the investigated range of parameters, while the pore diameter varied from 120 to 178 nm. Reflectance curves showed a wide range of low reflectance in the visible light region, which validates their applicability in the field of anti-reflection coatings.

1. Introduction

Research on non-standard fabrication processes for nanostructured materials has increased in recent years due to their unique properties which are quite different from the bulk form Ref. [1]. Nanomaterials have diverse applications including chemical sensing and biosensors [2], oncology [3], DNA translations [4], renewable energy [5] and many more. Well-ordered nanostructures have been fabricated using several techniques such as photolithography [6], X-ray [7], ion-beam [8] and interference lithography [9]. However, these techniques require expensive laboratory equipment.

Porous anodic aluminium oxide (AAO) has attracted a lot of attention due to its self-ordering properties as well as low cost of production [10]. AAO membranes can be used as a template for producing other nanostructures of different sophisticated materials. This can be achieved by depositing these materials into the pores by using several methods such as electrodeposition [11], sol-gel technique [12], atomic layer deposition [13] and chemical vapor deposition [14].

An important application of AAO is in the optical domain. Due to the high band gap of aluminium oxide, the material is transparent in the visible range, and it can be used as antireflection coating. Yang et al. have recently shown that the use of AAO in double-layer anti-reflection coating could increase the efficiency of GaAs solar cells [15]. Due to the porosity, the effective refractive index of AAO can present different values [16], which provides an additional method for controlling its reflectivity. For this reason, it is important to achieve an accurate control on the porosity and hole diameter of the AAO films. Moreover, the graded structures in AAO can be transferred to other materials, conferring them anti-reflective properties [17]. Masuda and Fukuda proposed a two-step

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anodization method, which relies on the use of a long process with oxalic acid and then phosphoric, and it results in well-ordered nanoporous membranes [18]. Since then, several researchers have keyed into two-step processes [19–22], mostly with a hard anodization followed by a mild one. As a result of this, the behaviour of AAO formed from one-step anodization process has been paid little attention due to its non-uniform and disordered pores [21]. However, for industrial applications, the one-step anodization process is a cheaper and less time consuming option.

Porous AAO has also been of significant importance in membrane technology [23–26]. Belwalka et al. showed the effects of applied voltage and electrolyte concentration on the nanopore parameters using sulphuric and oxalic acid electrolytes. The pore sizes ranging from 11 nm to 24 nm, which are applicable for ultrafiltration applications, were obtained and found to increase with increased voltage and decreased electrolyte concentration [24]. Huang et al. proposed that at lower potentials (< 17.5 V) in sulphuric acid, AAO membranes for nanofiltration applications such as haemodialysis can be fabricated [25]. Microfilters, however, require weaker acids (phosphoric acids) which produce larger pore sizes [27].

Porous AAO is formed through an electrochemical process in which there is an increase in the thickness of the oxide layer on the surface of the aluminium metal [28]. Acidic electrolytes such as oxalic, sulphuric and phosphoric acids are usually used and the oxide growth rate depends on the anodization voltage, electrolyte concentration and electrolyte temperature [21–31]. The best alumina pore uniformity and circularity are obtained at very low temperatures (1 °C–5 °C) [29].

In this work, nanoporous AAO membranes were fabricated andthe effects of anodization potential and concentration of phosphoric acid on nanoporediameters, interpore distance and porosity were investigated for the one-step anodization with phosphoric acid. The reflectivity of the obtained membranes was also obtained to determine its suitability as antireflection coating.

2. Experimental

High purity (99.96%) aluminium foil of 0.05 mm thickness cut into dimensions of 12 mm by 5 mm were first degreased in acetone and then cleaned in a mixed solution of HNO_3:HCl:H_2O in a volumetric ratio of 10:20:70. These cleaned foils were then annealed at 400^0C in Nitrogen atmosphere for 30 min. The aluminium foils (anode) were mounted on a copper holder, while a gold coated glass was used as counter electrode. The holder was then placed on the beaker containing the electrolyte in such a way that only the electrodes are immersed with no part of the copper holder touching the solution. The anodization process took place for 10 min in a solution with phosphoric acid electrolyte (1–5%). The concentration and cell potential were varied. The electrolyte temperature was maintained at about 3^0C by placing the beaker into an ice bath as shown in Fig. 1.

The morphology of the formed oxide was observed using a Scanning Electron Microscope (SEM). The program Image J was used in measuring the pore diameter, interpore distance, porosity and thickness of the nanotubes. In order to do this, a SEM image of a random location of the sample was opened with the software. The pores were isolated using the “threshold” tool and the area of each hole was measured automatically by the program. The average pore diameter was calculated from the average pore area obtained using the formula for the area of a circle. The porosity has been defined as the percentage of the area that is occupied by holes, and it has been calculated by dividing the total area of the holes measured by the area of the sample section being studied. The interpore distance, defined as the distance from the centres of two adjacent pores, was measured by using the manual tool “length measurement” from the software. An averaged number of 150 holes and 100 interpore distances per sample were measured to obtain a statistically relevant mean. The thickness of the oxide films have been obtained by SEM imaging of the cross-sectioned samples.

Fig. 2 shows the schematic diagram of the used reflectance measurement set up. The light source consists of an Oriel 77,501 Fibre Optics Illuminator which transmits the light through a Spectral Product CM110 1/8 m monochromator which then passes on a selectable range of light wavelength. The detector is used to obtain the relative intensity of reflected light. This is then normalised using polished pure aluminium as a reference and converting to reflectivity using aluminium reflectivity obtained from literature [32].

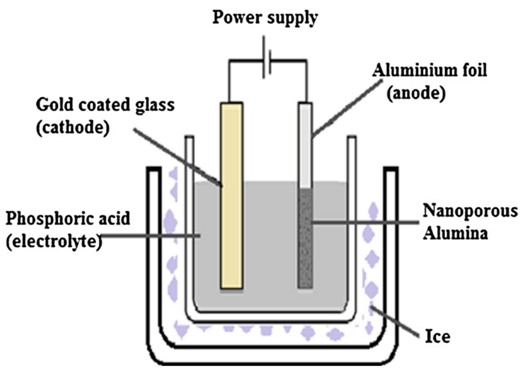

Fig. 1. Schematic diagram of anodization set-up.