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Nanoporous thin films obtained by oblique angle deposition of aluminum on porous surfaces

R.J. Santos[a,*], A. Chuvilin[b,c], E. Modin[d,e], S.P. Rodrigues[a,f], S. Carvalho[a,f], M.T. Vieira[a]

[a] CEMMPRE, Mechanical Engineering Department, University of Coimbra, 3030-788 Coimbra, Portugal
[b] CIC nanoGUNE Consolider, 76 Tolosa Hiribidea, Donostia-San Sebastian 20018, Spain
[c] IKERBASQUE Basque Foundation for Science, 3 Maria Diaz de Haro, Bilbao E-48013, Spain
[d] National Research Centre "Kurchatov Institute", Kurchatov Sq. 1, Moscow, Russia
[e] Far Eastern Federal University, 8 Sukhanova st., Vladivostok 690000, Russia
[f] CFUM-UP, Physics Department, University of Minho, 4800-058 Guimarães, Portugal

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ABSTRACT

The oblique angle deposition (OAD) is a versatile and easily controllable method appropriate for the production of nanoporous structures with pores in nanometric range and high surface area. In this study, aluminum thin films were deposited by sputtering on both commercial and homemade porous aluminum oxide substrates, tilted 85° and 89°. The morphology of substrates and the shadowing effect created by the OAD led to the deposition of densely packed columnar Al thin films with surface pores which sizes range between 19 and 75 nm depending on the substrate, tilt angle, time of deposition and power density. Focused ion beam (FIB) nanotomography allowed the 3D reconstruction of the whole nanoporous structures, in which the substrate, the thin film and the interface could be easily observed. Moreover, these results showed the hourglass-like shape of pores in the Al thin films, as well as the pores interconnectivity and the existence of open porosity that ensures the passage of the gas/liquid flow through the nanoporous structure. This study provides further insights into the production patterns of nanoporous structures by OAD, with a potential application in nanofiltration systems able to filter nanoparticles, which are often found in industrial environments and can represent a risk for human health and environment.

1. Introduction

Nanoporous structures (pore size < 100 nm) with unique characteristics, namely with high surface area and small pores diameter, have generated significant interest in many applications, such as catalysis [1], biomedical devices [2], sensors [3], energy storage [4] and filters [5].

A wide range of materials can be used to manufacture nanoporous structures by either subtractive processes which are based on material etching (e.g. chemical, electrochemical and e-beam) or by additive processes consisting of surface deposition (e.g. chemical or physical vapor depositions, pulsed laser deposition and sol-gel) [6]. Among them, physical vapor deposition of thin films with the substrate tilted (Oblique Angle Deposition (OAD)) is becoming the process of choice, since its advantages overcome its drawbacks: it is a scalable and environmentally friendly fabrication method, compatible with various materials, which enables creating of diverse nanostructured morphologies.

Since the mid-twentieth century, OAD has been a widely used technique to produce porous morphologies [7–9]. Nowadays, OAD is a common approach used for deposition of nanocolumnar thin films with nanoporosity for many applications, ensuring the easy control the thin films morphology and porosity through adjustment of the deposition parameters. By taking advantage of the shadowing effect, which is created by growing columns when the substrate is tilted, OAD introduces significant porosity on the thin film [10]. In fact, the tilt angle, α, influences the shadowing effect and consequently the size of pores and columns. Previously, it has been reported [11,12] that with the increase of α, the pore size grows and isolated columns start to appear. Other parameters, such as deposition time (film thickness) [13,14], deposition rate [15], deposition pressure [16] and gas composition [17], also may have the influence on the morphology of thin films deposited by OAD, although sometimes no direct correlation with morphology can be found [18].

The nanoporous structures applied in filtration devices, require a structure with open porosity through the whole membrane thickness. In order to fulfill this requirement, porous substrates are usually used as starting materials for the deposition of nanoporous thin films by OAD.

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[*] Corresponding author.
E-mail address: rita.santos@dem.uc.pt (R.J. Santos).

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These substrates give rise to nanoporous thin films with morphologies and porosities differing from those deposited on bulk substrates at the same conditions. The porous structure of substrate leads the material to be preferably deposited on protruded regions (pore walls), initially forming "islands" that continue to grow with the deposition time. Afterwards, these "islands" coalesce forming a highly porous columnar structure. Therefore, the pores are firstly created by the shadowing effect promoted by the prominent pore walls of the porous substrate and then by the growing of columns that prevent the deposition of the material behind them.

Zhou and *Gall* [13] have sputtered Ta and Al thin films at $\alpha = 84^\circ$ on Si pit-array patterns, demonstrating the decrease of the porosity with the film thickness. Nevertheless, the effects of other deposition parameters on the characteristics of the Ta and Al nanoporous thin films have not yet been investigated. In other study [19], Al and W were deposited by rf magnetron sputtering on porous anodized aluminum at $\alpha = 85^\circ$. The adatoms were preferably deposited over the hexagonal structure of substrates and the increase of the deposition time caused the broadening of nanorods and consequent narrowing of the pores. These results highlight the importance of the substrate morphology for achieving the desired nanoporous structure.

Besides the high potential of OAD for fabrication of nanoporous membranes, the research in this field is quite limited. In particular, the influence of some deposition parameters on the pores structure and interconnectivity is so far unexplored. The knowledge of these characteristics, being of key importance for nanofiltration applications, requires the utilization of advanced characterization techniques. In this sense, this study reports a simple and scalable method to control the pore size of nanoporous structures suitable for nanofiltration purposes with a posterior characterization through advanced techniques. The nanoporous structures are produced using the OAD method, by sputtering aluminum thin films on porous aluminum oxide substrates. The effects of the substrate morphology, deposition time, tilt angle α and power density on the morphology and porosity of nanoporous structures, are studied. Scanning electron microscopy (SEM) has allowed the visualization of the surface morphology of nanoporous thin films. The sizes of surface pores and columns have been estimated by image processing and analysis. In depth, 3D characterization of pores has been performed by focused ion beam (FIB) nanotomography, which allows to assess the internal structure of thin films, such as the size, shape and interconnectivity of pores, through the reconstruction of 3D images.

2. Materials and methods

Aluminum thin films were deposited by rf magnetron sputtering using the OAD method onto commercial and homemade porous aluminum oxide substrates. Commercial aluminum oxide substrates were Anopore (Whatman® Anopore) with a diameter of 13 mm and a thickness of around 60 μm. Homemade aluminum oxide substrates (AAO) were produced by anodizing an Al 6016 alloy surface by the following procedure.

Aluminum pieces ($20 \times 20 \times 1\ \text{mm}^3$) were mechanically grinded until the 2400 grit size, finished with mirror-like polishing with 3 μm diamond paste. Afterwards, aluminum pieces were anodized in a two-steps procedure, both steps been performed at the same conditions. In the first step, the anodization was conducted in a stirred 5 wt% H_3PO_4 (phosphoric acid) electrolyte solution at 273–278 K (electrochemical cell in an iced bath) during 60 min. A DC power supply (Agilent Technologies, N5751A model, max. 300 V, 2.5 A) was working on potentiostatic mode at a constant voltage of 100 V, allowing the current passage through the electrolyte, between the graphitic rod (cathode) and the aluminum alloy surface (anode). Then, the Al alloy was chemically etched (8 wt% H_3PO_4 + 4 wt% CrO_3) at 333 K for 30 min, to selectively remove the initial disordered oxide layer typical for the first anodization, and finally washed in a ultrasonic bath for 10 min. This step resulted in semi-spherical pits that served as seeds to grow the ordered Al oxide pores in the second anodization. After the second anodization, an ordered porous structure of Al_2O_3 with about 2 μm of thickness, was produced.

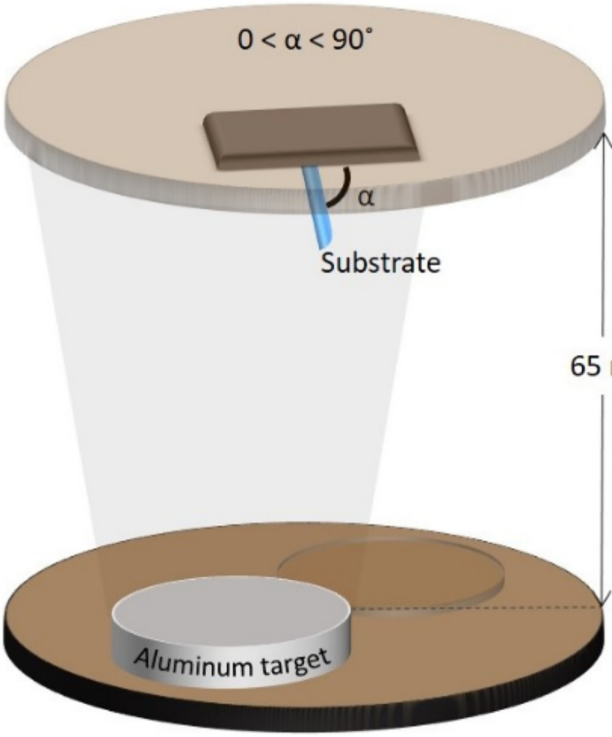

Fig. 1. Experimental setup.

The OAD by rf magnetron sputtering of nanoporous aluminum thin films, on Anopore and homemade AAO, was performed using a sputter coating system (Fig. 1). OAD was carried out at 0.7 Pa in a 99.999% Ar atmosphere, the substrates were tilted at $\alpha = 85^\circ$ and 89°. Al target was used to deposit the thin films at 1.27×10^4 and $3.18 \times 10^4\ \text{W/m}^2$ for 60 min and at $2.55 \times 10^4\ \text{W/m}^2$ for 30, 60 and 90 min.

The surface and cross section morphologies of the nanoporous structures were analyzed by SEM (FEI Quanta 400 FEG) at an accelerating voltage of 15 kV. Micrographs of the surface were then processed and analyzed by the ImageTool 3.0 software. The average size of pores and columns found by manual threshold at the top surface of thin films were determined by estimating the Feret diameter.

The FIB Slice and View 3D imaging was performed using a dual-beam system FIB/SEM (FEI Helios 450S Dual Beam™), which enabled the 3D reconstruction to assess the whole internal structure, including pore size, shape and interconnectivity. The nanoporous structures, precoated with a 150 nm Pt protective layer, were sectioned parallel to the top surface, removing slices one by one with the FIB working at an accelerating voltage of 30 kV and with a beam current of 18 pA (Fig. 2). The image of each section was successively acquired by SEM (accelerating voltage: 5 kV; current: 100 pA) in a high resolution mode. This process was run in a fully automated mode using the AutoSlice&View™ G3 software. Thus, acquired 3D data cube was further processed, visualised and quantified in FEI VSG Avizo software.

3. Results and discussion

3.1. Morphology

The aluminum thin films were deposited on two different porous substrates (Anopore and AAO) by OAD with the substrates tilted at $\alpha = 85^\circ$ and 89°. Porous substrates (Fig. 3) show different morphologies, with different pore diameter, pore shape and walls thickness.