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Advanced morphological analysis of patterns of thin anodic porous alumina

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ABSTRACT

Different conditions of fabrication of thin anodic porous alumina on glass substrates have been explored, obtaining two sets of samples with varying pore density and porosity, respectively. The patterns of pores have been imaged by high resolution scanning electron microscopy and analyzed by innovative methods. The regularity ratio has been extracted from radial profiles of the fast Fourier transforms of the images. Additionally, the Minkowski measures have been calculated. It was first observed that the regularity ratio averaged across all directions is properly corrected by the coefficient previously determined in the literature. Furthermore, the angularly averaged regularity ratio for the thin porous alumina made during short single-step anodizations is lower than that of hexagonal patterns of pores as for thick porous alumina from aluminum electropolishing and two-step anodization. Therefore, the regularity ratio represents a reliable measure of pattern order. At the same time, the lower angular spread of the regularity ratio shows that disordered porous alumina is more isotropic. Within each set, when changing either pore density or porosity, both regularity and isotropy remain rather constant, showing consistent fabrication quality of the experimental patterns. Minor deviations are tentatively discussed with the aid of the Minkowski measures, and the slight decrease in both regularity and isotropy for the final data-points of the porosity set is ascribed to excess pore opening and consequent pore merging.

1. Introduction

In recent years, electrochemical anodization of aluminum foils has attracted much interest as a means of fabrication of nanostructured surfaces of anodic porous alumina (APA) [1]. APA substrates have been used in nanofabrication (e.g. as lithographic masks [2–5] and templates for metallic [6], polymeric [7] or oxide [8] nanowires), in opto-electronic devices (e.g. as distributed feedback lasers [9], photonic crystals [10], SERS substrates [11] and Bragg reflectors [12]), in biology (e.g. as cell culture substrates [13–16] or membranes for drug delivery [17–19]), and in fundamental investigations of wettability [20–22]. With respect to conventional top-down nanofabrication based on optical and electron beam lithography, anodization can regularly pattern oxides of valve metals (Ti, W, Zr and Ta in addition to Al [23]) on large surfaces in cost and time-effective manner. The controlled anodization of Al is indeed a bottom-up nanopatterning technique, based on self-assembly of nanostructures arising from a combination of chemical reactions and physical processes, such as electrical conduction, diffusion and thermodynamics [24].

APA thickness of 10–50 μm can be obtained with standard two-step anodization [1], giving rise to locally close-packed

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hexagonally arranged cells, each containing an elongated pore. Patterns with reproducible pore size d and cell size D (with cell wall thickness $w = D - d$) can be obtained by setting a given anodization voltage in an appropriate acidic aqueous electrolyte, while keeping constant the bath temperature and stirring rate [1]. Optimized anodization results into a narrow pore size distribution (13% ratio of standard deviation to mean size), which is considered monodisperse as compared to the similarly obtained porous silicon [25,26]. However, pore and cell size, and their ratio defined here as pore filling factor $f = d/D$, are not the only important geometrical parameters. In some applications, especially in the field of opto-electronics [9,10], the ordered position of the pore centers is also important. Additionally, fabrication processes far from optimal conditions (e.g. at current density $j \geq 100$ mA/cm^2) can give rise to non-circular and irregularly placed pores.

Thin APA (~100 nm) can be obtained by anodizing thin layers of Al previously deposited on a substrate. The fabrication of such thin films is of particular interest in applications such as the coating of permanent implants for orthopedics or dentistry [27] and the fabrication of top functional layers in sensors based on either mechanical [28] or spectroscopic properties [11]. The use of silicon and glass wafers as the substrates allows to start from highly planar surfaces that can be conveniently integrated into standard microfabrication processes. Moreover, since porous alumina is transparent in the visible part of the electromagnetic spectrum, using glass for living cell cultures makes optical transmission microscopy possible.

Since an efficient control of both size and spatial organization of the nanostructures is important in practical applications, a deep understanding of the thin APA patterns is required. In former works successful use of regularity ratio (RR) for APA patterns has been demonstrated on thick APA made from aluminum foils (thickness ≥ 10 μm) [29,30]. In this work we report for the first time the application of RR to patterns of thin APA fabricated on glass substrates. We define more precisely the concept of average RR and introduce the associated RR angular spread for the evaluation of the pattern isotropy. Additionally, we calculate the analytical quantities called Minkowski functionals, taken from the field of integral geometry [31]. Both analytical tools are applied to thin APA for the first time, after their preliminary test on artificial patterns made by computer aided design (CAD) to check for the agreement between theory and experiment.

2. Materials and Methods

2.1. Fabrication of Thin APA

Al films with ~100 nm thickness were deposited by an electron-beam evaporator (PVD75, Kurt J. Lesker Ltd., UK) on glass substrates of 2 inch wafer size (base pressure 10^{-6} Torr, deposition rate 0.3 Å/s). Anodizations were carried out in a home-designed Teflon cell in aqueous solutions of different acids (0.3 M oxalic acid or 0.4 M phosphoric acid) at a constant voltage (between 40 and 110 V). Due to the small Al thickness, 30–40 s long anodizations were sufficient to oxidize the whole Al film (a typical chronoamperometric curve is shown in Fig. S1). The obtained pores were widened by wet-etching in 9 wt.% aqueous phosphoric acid at room temperature (RT). By increasing the etching time (typically between 0 and 45 min) APA films with constant D and increasing d were obtained. All used chemicals were from Sigma-Aldrich (Italy).

2.2. SEM Imaging

The thin APA surfaces were imaged by a high-resolution scanning electron microscope (SEM, JSM-7500F, Jeol, Japan) equipped with a cold field-emission gun, collecting the secondary electrons resulting from a 5 kV primary beam. Two standard magnifications of 50 and 100 kX were used, the former to obtain an overview of a large sample area and check against major defects, and the latter to acquire the image to be analyzed. We avoided surface coating with a conductive drain layer as we did not want to modify the APA morphology. As a consequence, the S/N ratio was not always optimal due to static electrical charging, but the disturbances could be minimized when pre-processing the images as explained in the next section.

2.3. Digital Image Formats

All SEM images were 1280 × 960 pixels (px), which in all cases allowed for sampling the pore area with at least 400 px. The grayscale intensity was coded in 8-bit values. To avoid erroneous assignment of single pixel noise to tiny pores, the images were low-pass filtered with a spatial kernel filter of Gaussian profile and 2 √px radius, by means of Photoshop CS5 (Adobe Systems Inc., USA). The intensity levels were corrected by contrast equalization, such as to better span the 256 levels of brightness available and limit the differences in results among different SEM work-sessions. To estimate the morphological parameters of the APA patterns, the pre-treated SEM images were analyzed using the grain analysis tool of Igor 6.22 (Wavemetrics, USA). The d and D values, along with the respective standard deviations, were estimated by averaging the values from three different SEM images of the same representative sample. In each image the number of pores n and cells N ($n = N$) was ≥100.

To test the effect of both the RR and Minkowski analyses on porous patterns, prior to their application to experimental SEM images of thin APA we performed the same characterization on artificial images of ideal porous patterns. These images were generated by CAD tools of CorelDRAW 9 (Corel Corporation, Canada). Two sets of ideal images have been generated, with black circles (pores) on white background (cell wall top). In one set the circles have both increasing d and D, at constant $f = 0.5$. Since increasing D means decreasing the number of cells N (i.e. the number of pores n), the pore density $\sigma = n/A$ (with A the image area) decreases, and we call this shortly the (decreasing) pore density set (or σ set).

In another set of images only d is increased while keeping D constant, which increases f. Since porosity can be defined as $p = A_{pore}/A = nA_{pore}/NA_{cell} = A_{pore}/A_{cell} = d^2/D^2 = f^2$, we call this shortly as the (increasing) porosity set (or p set). In both σ and p sets A was kept constant, different from a previous work [29].

Since the Minkowski analysis requires gray level images, the CAD image format was changed from B/W (1 bit) to 256 gray levels (8 bits), and the two single gray levels of interest,