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Characterization of nanopores ordering in anodic alumina

Stefan Mátéfi-Tempfli *, Mária Mátéfi-Tempfli, Luc Piraux

Unité de Physico-Chimie et de Physique des Matériaux, Université Catholique de Louvain, Place Croix du Sud, 1, B-1348 Louvain-la-Neuve, Belgium

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Abstract

A simple characterization method of the ordering of the nanopores is described for nanoporous anodized aluminium oxides. The method starts with image analysis on scanning electron microscopy representations for the purpose to find repetitive shapes and their centres, i.e. nanopores. Then triangles defined by coordinates of the centres are identified by Delaunay tessellation. Evaluation of the ordering degrees is then performed by a two-level analysis of the triangles. We define order parameters for triangular and hexagonal organization levels and show through typical examples that they are highly sensitive on ordering.

Keywords: Degree of ordering; Nanoporous alumina; Delaunay tessellation

1. Introduction

Nanoporous anodic aluminium oxide (AAO) films prepared by electrochemical oxidation of the aluminium foils are known since many years [1–4]. They are stable at high temperatures and in organic solvents, and pore channels are uniform, parallel to each other and perpendicular to the surface. Such AAO films have found various application areas, i.e. for the fabrication of nanowires with a variety of compositions and complex structures [5], for the fabrication of ordered carbon nanotubes arrays [6], as potential media in high density magnetic storage [7] and many others.

Starting with the discovery of the self-ordering phenomena by Masuda and Fukuda [8], we know that during pore growth in AAO, the pore tips evolve to an ideally hexagonally ordered arrangement. Systematic studies in this respect show that the degree of ordering could be influenced by the preparation conditions, i.e. anodization time, electrolyte type and its pH, applied voltage and temperature, see for example [9]. Perfect regularity could be obtained by prepatterning the aluminium surface before anodization [10] with various techniques, like e-beam lithography or nanoindentation. Despite of the perfect uniformity achieved by such methods, they remain costly alternatives of the simpler one, which is just based on the self-ordering phenomena. The preparation of highly ordered AAOs based on self-ordering is more accessible because of its easy and low-cost processing. To understand this phenomenon and better control the degree of ordering, we require characterization tools to evaluate them in a simple but objective manner.

One of the simplest ways for a qualitative analysis is the visual inspection but this method is highly influenced by subjectivism and, in consequence, is largely unsatisfactory. Better qualitative analysis could be done by 2D Fourier Transformation but it does not give acceptable results for short-range ordering. An objective and quantitative analysis of the degree of the ordering is most appropriate.

Order determination for 2D arrays dates back to late ’70s with the development of the Kosterlitz–Thouless–Halperin–Nelson–Young (KTHNY) theory of 2D melting [11–14]. A large number of experiments and simulations have been performed to test the KTHNY theory. Unfortunately, the results are sometimes contradictory [15,16]. The theory defines a translational correlation function and an orientational one for the characterization of the 2D systems. However these functions characterize quite well 2D translational and orientational ordering, see for example [17,18], their calculus is laborious.

Few attempts have been made to propose order parameters based on different approaches. Using Voronoï tessellation [19],

* Corresponding author.
E-mail address: matefi@pcpm.ucl.ac.be (S. Mátéfi-Tempfli).

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Lim et al. [20] show a model of pores growth and Randon et al. [21] calculate a surface coverage ratio of polycrystallites with hexagonal symmetry. Radial distribution functions where used to characterize ordering [9,22,23] and order parameters for 1D and 2D ordering, based on them, were proposed by Behnke et al. [24]. The above-mentioned models deal with hexagons and polygons. We believe that on a "first-level" analysis of the 2D self-ordered nanoporous alumina, the lowest symmetry to be considered is not a hexagonal one but a triangular one. Hexagonal and more generally polygonal shapes should be considered only on a "second-level" analysis because they are superstructures of the more elementary triangular shape.

In this paper, we present a new analysis method based on a Delaunay tessellation [25] and calculate some parameters that characterize the self-ordered alumina. We define two order parameters, one for a triangular and another for a hexagonal symmetry, and show that they are highly sensitive on ordering.

2. Ordering characterization

In our approach, a SEM image from the self ordered structure, i.e. AAO, see Fig. 1(a), is examined using a procedure implemented in IgorPro, a scientific data analysis program from WaveMetrics, Inc. (Portland, OR, USA). While the program is easy to use, it is also very powerful to solve complex data processing tasks permitting us to implement not only the ordering analysis of the present work but also many difficult problems of previous works, i.e. time–frequency spectral analysis by Gábor transformations [26,27].

According to this method, we first define a rectangular region of interest (ROI) on the image avoiding labels, texts and sides. In a general manner, we have several preliminary informations from the sample and from its image. For instance, considering nanoporous alumina, we can presume its approximate interpore distance, being in relation with its preparation conditions. We know or we could determine easily parameters of the SEM image such as zoom, resolution and correspondence between pixels and physical distances on the image. All of these data will help us during the analysis. In this respect, we define the ROI spaced from labels, texts and sides with the half of the presumed interpore distance in order to avoid undesirable side effects.

Then, a particle analysis is performed using functions of the image analysis package of the above-mentioned program. A correct choice for the threshold value (or method in case of an automatic threshold method) is essential in order to identify correctly the pores. Because SEM images could be very different from each other in contrast and brightness, it is difficult to define a unique and automated method to perform this identification. The most adequate method is a try-and-repeat cycle until best identification is obtained, trying between different methods available in the image analysis package. For the SEM image presented in Fig. 1, we chose an automatic fuzzy thresholding using entropy as the measure for "fuzziness". The particle analysis identifies pores, their contours and their centres, see Fig. 1(b).

The coordinates of the centres of the pores, obtained by this way, serve as starting point for geometrical and subsequent ordering analysis. We use a triangulation method based on a Delaunay tessellation [25] obtaining triangles between centres of the pores, see Fig. 1(c). As we have already expressed above, we consider that a better approach for the ordering analysis is to

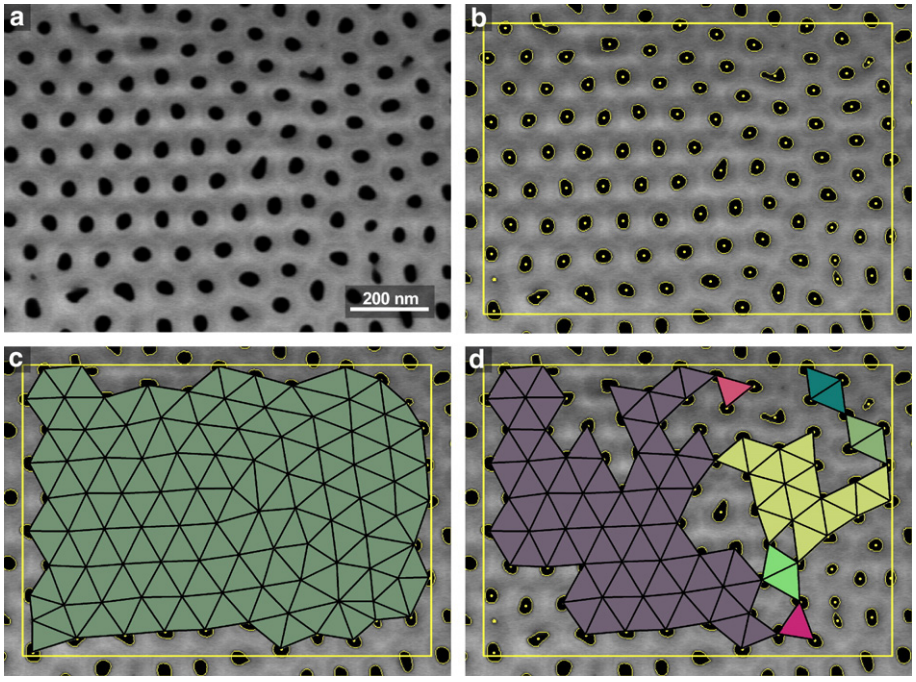

Fig. 1. Scanning electron micrograph (a) from nanoporous alumina anodized in oxalic acid at 40 V. Pores, their contours and their centres inside a region of interest (b) recognized by particle analysis. Triangles between centres of the pores (c) by Delaunay tessellation. Groups of more regular triangles (d) identified as being within a 10% of error band.