

SURFACE MORPHOLOGY ANALYSIS AND NANOPOROUS STRUCTURE QUANTIFICATION BY DIGITAL PROCESSING OF SEM IMAGES OF ANODIC ALUMINIUM OXIDE FILMS

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Abstract: The morphology of the surface of thin nanoporous anodic aluminum oxide films on SiO₂/Si substrates formed in oxalic, sulfamic and malonic acid at 20 V was studied by means of SEM. SEM images were processed with ImageJ allowed to calculate the parameters of the nanoporous structure. It is shown that for the studied anodic films, the inter-pore distance (cell size) was independent of the anodizing acid. The obtained results indicate that mechanical stress in anodic films, which is occurring during anodizing, is due to large volume expansion control of growth of the nanoporous structure.

Keywords: anodic alumina; surface morphology; nanoporous structure; interpore distance; stress-driven transport.

1. Introduction

The current stage in the development of science is characterized by a rapid progress of nanotechnologies, aimed at systemic studies of nanoscale objects and production of new nanomaterials with improved properties. It is well known that properties of nanomaterials depend on the size of nanoparticles. Therefore, obtaining nanomaterials with precise control and analysis of size distribution of nanoparticles is one of the vital tasks in nanotechnology. Morphology analysis of the surface of nanomaterials is used to control and determine nanosizes. The purpose of such an analysis is statistical processing of data obtained from measurements, plotting graphical dependencies to visualize the analysis process and determining the average values of the measured characteristics. Currently, nanoporous aluminium oxide films are considered as a promising material for numerous nanotechnology applications because of their suitability being a template in many of them. Films of amorphous anodic alumina with highly ordered cell-porous structure are formed on the surface of aluminum, when anodizing takes place in aqueous solutions of acids, such as sulfuric, oxalic or phosphoric acid [1]. High reproducibility of oxide parameters (pore and cell diameters, pore density) allows applying

nanoporous alumina films in magnetic recording, electronic and electro-optical devices [2-5].

Major properties of anodic alumina films are defined by such a structural parameter as the pore diameter. Statistical methods of analysis allow to process big arrays of nanosized pores and design algorithms for studying peculiarities of their morphology. Investigations of nanoporous structure are therefore of a significant practical importance.

The aim of this work was to analyze the formation of the surface morphology of nanostructured anodic aluminum oxide films, obtained by electrochemical anodizing of aluminium in three electrolytes: oxalic, sulfamic and malonic acid at the same voltage. The reason for choice of such types of the electrolytes was the necessity to obtain porous anodic alumina films with different surface morphology. SEM surface images of nanoporous alumina films were used for analysis of morphology using the ImageJ software and obtaining quantitative information on the distribution of pore sizes and inter-pore distances.

2. Experimental

Aluminium films of about 100 nm in thickness were obtained on SiO₂/Si substrates by vacuum thermal evaporation. Pieces of 2 × 2 cm² were cut and anodized at a constant voltage of 20 V in a

0.3 M oxalic acid, 1.5 M sulfamic acid and 0.8 M malonic one. The anodizing area of ca. 0.22 cm² was set out by a Viton o-ring. The process was carried out in two electrode polytetrafluoroethylene cell at a constant temperature of (20 ± 0.1) °C.

A scanning electron microscope (SEM) model DSM 982 (Zeiss) was used for investigating the surface morphology of the thin anodic alumina films. SEM images were processed by ImageJ (Figure 1). The results were used to determine the mean diameter (d_{pore}) of the pores. The curves of the pore size distribution were fitted by Gaussian curves.

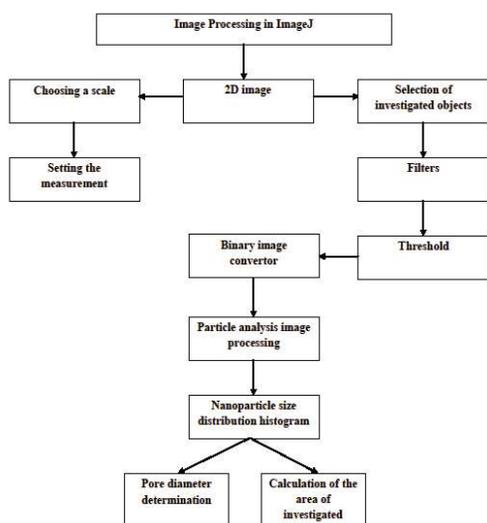


Figure 1. Scheme of the processing of surface morphology images of nanoporous anodic aluminium oxide films in ImageJ.

According to the initial pore size distribution it was assumed to involve both incipient pores of a small diameter and major pores of a large diameter. Incipient pores were excluded from calculations, as only data on the major pores are of practical importance and the presence of the incipient pores misrepresents the results of the analysis. At the same time, for proper Gaussian fitting of the curve to present the pore size distribution, one point before the maximum was used for the analysis. The maximum in the pore size distribution curve corresponded to the d_{pore} .

3. Results and discussion

In nanoporous anodic alumina films formed in oxalic acid on the SiO₂/Si substrate, the pore

diameter was 15.3 nm (Figure 2) and the value of the inter-pore distance was 62.5 nm (Table).

Table The inter-pore distance (D_{inter}), pore diameter (d_{pore}) and wall thickness per volt for porous anodic alumina films formed in various anodizing electrolytes at 20 V.

Electrolyte	0.3 M oxalic acid	1.5M sulfamic acid	0.8M malonic acid
d_{pore} , nm	15.3	16.5	16.3
D_{inter} , nm	62.5	62.3	63.0
Wall thickness per volt (nm V ⁻¹)	1.18	1.15	1.17

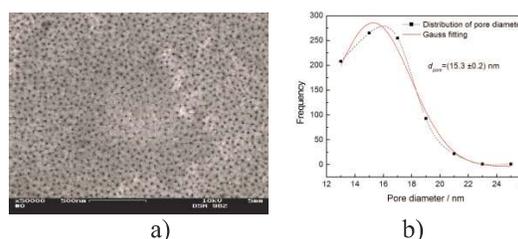


Figure 2. SEM image of the surface of porous alumina film on SiO₂/Si substrate formed in oxalic acid solution at 20 V (a). The distribution of pore diameter calculated by ImageJ (black) and Gauss fitting (red) are represented on the right (b).

Data on the parameters of the microstructure of porous anodic aluminum oxide films obtained in oxalic acid at 20 V in our work are in agreement with the results in [7]. In case of nanoporous alumina films obtained in sulfamic acid on the SiO₂/Si substrate, the d_{pore} was equal to 16.5 nm (Figure 3) and the D_{inter} value stood at 62.3 nm (Table).

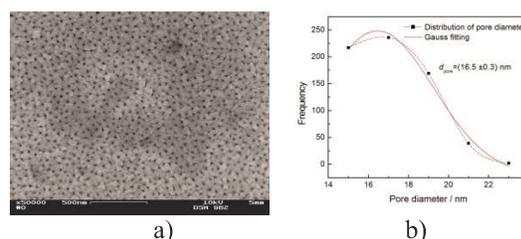


Figure 3. SEM image of the surface of porous alumina film on SiO₂/Si substrate formed in sulfamic acid solution at 20 V (a). The distribution of pore diameter calculated by ImageJ (black) and Gauss fitting (red) are represented on the right (b).

Films of nanoporous alumina formed in malonic acid on the SiO₂/Si substrate were characterized by the value of d_{pore} amounting to 16.3 nm (Figure 4) and the D_{inter} value of 63.0 nm (Table).

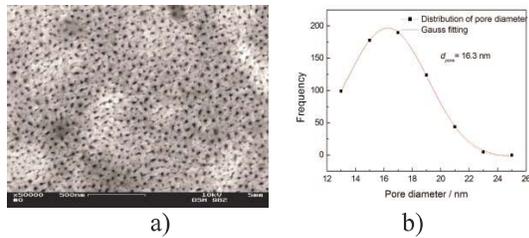


Figure 4. SEM image of the surface of porous alumina film on SiO₂/Si substrate formed in a malonic acid solution at 20 V (a). The distribution of pore diameter calculated by ImageJ (black) and Gauss fitting (red) are represented on the right (b).

It is generally accepted that the geometric microstructure of the formed films of porous anodic aluminium oxide is determined by such parameters of the anodizing process as the type of anodizing acid and anodizing voltage applied. An important characteristic of the microstructure of the anodic film in the electrolyte-dependent anodizing is the thickness of a pore wall per 1 V voltage. The thickness of pore wall (W) of anodic films can be determined using the equation: $W = (D_{\text{inter}} - D_{\text{pore}})/2$. The values of wall thickness of pores per 1 V calculated for oxalic, sulfamic, and malonic acids are represented in the Table. It should be noted that the results obtained are in good agreement with the data in [1].

The obtained results show that the inter-pore distance (cell size) of the anodic alumina films does not depend on the anodizing acid. At the same time, anodic films obtained in these electrolytes had different pore diameters. We assume that in addition to the anode potential, mechanical stresses may be a common factor for forming anode films. In this case, the mechanical stresses in anodic films, which are occurring during anodizing due to large volume expansion do control the growth of the nanoporous structure, regardless of the anodizing acid. According to [8], significant volume expansion is taking place during growth of porous anodic alumina. The ratio of the oxide thickness formed to the aluminum thickness consumed reached 1.22 for anodizing in oxalic acid at 20 V, which indicates a large extent of volume expansion. This is in agreement with stress-driven transport in the ordered porous anodic films, where Al³⁺ and O²⁻ ions are transported by means of electrical migration and viscous flow [9]. As it was shown by tracer

experiments [10] and simulations in [9], oxide is flowing from the thin layer at the pore bottoms outwards to the space between pores.

4. Conclusions

The pore diameter distribution and the mean pore diameter of the nanoporous alumina films were calculated from the SEM images using ImageJ software. The processed results allowed us to calculate the value of the mean pore diameter of anodic alumina films obtained in oxalic, sulfamic and malonic acids. It was shown that statistical methods are simple and very informative methods for studying the nanoporous structure of anodic alumina films.

It was demonstrated that inter-pore distance (cell size) in porous anodic alumina films is independent of the anodizing acid. At the same time, the anodic films formed in different electrolytes had different pore diameters. Based on the obtained results, it was concluded that mechanical stresses in anodic films, which are occurring during anodizing, are due to a large volume expansion, controlling the growth of the nanoporous structure regardless of the anodic acid.

References:

- [1] G.D. Sulka, *Nanostructured materials in electrochemistry*, Ed. A. Eftekhari (Wiley, 2008) 1.
- [2] W. Lee, S.-J. Park, *Chem. Rev.* **114** (2014) 7487.
- [3] T. Kikuchi, O. Nishinaga, S. Natsui, R.O. Suzuki, *Appl. Surf. Sci.* **341** (2015) 19–27.
- [4] A. Brzózka, A. Brudzisz, K. Hnida, G.D. Sulka, *Electrochemically Engineered Nanoporous Materials. Springer Series in Materials Science*, Eds. D. Losic, A. Santos (Springer, Cham, 2015) 219–288.
- [5] I. Vrublevsky, K. Charniakova, V. Videkov, A. Tuchkovsky, *Nanosci. & Nanotechn. – Nanostructured materials application and innovation transfer*, **16** (2016) 42–43.
- [6] A. Baron-Wiecheć, M.G. Burke, T. Hashimoto, H. Liu, P. Skeldon, G.E. Thompson, H. Habazaki, J.-J. Ganem, I.C. Vickridge, *Electrochim. Acta.* **113** (2013) 302–312.
- [7] S. Ono, N. Masuko, *Surf. Coat. Technol.* **169**–**170** (2003) 139–142.
- [8] I. Vrublevsky, V. Parkoun, J. Schreckenbach, G. Marx, *Appl. Surf. Sci.* **227** (2004) 282–292.
- [9] J. Houser, K. Hebert, *Nat. Mater.* **8** (2009) 415–420.
- [10] S. Garcia-Vergara, P. Skeldon, G. Thompson, H. Habazaki, *Electrochim. Acta.* **52** (2006) 681–687.