Measurement of Physical Properties of Anodized Al₂O₃
FESEM Images

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ABSTRACT
The objective of the proposed study is to develop an automated tool to determine the effect of time on nanopore structures. The designed tool extracts the nanopores from the Al₂O₃ FESEM images and computes their geometrical and statistical features. These values are further used to measure the variance of wall thickness and nanopore size which depend on four prominent anodizing parameters, namely, concentration (%), time (min), temperature (°C) and voltage (V). It is found that the structure and regularity of the nanopore arrangement is significantly improved by increasing anodizing time (min) at constant concentration (%), temperature (°C) and voltage (V). It is also observed that, after the anodizing process at every interval of time there is a significant decrease in wall thickness from 58 nm to 41 nm and increase in nanopores size from 32 nm to 78 nm. The experimental results are compared with the manual results obtained by the chemical expert and demonstrate the efficacy of the proposed method.

General Terms
Algorithms, Al₂O₃, Nanotechnology.

Keywords
Aluminium nanopore, Computational chemistry, Nanopore image analysis, Image segmentation, FESEM, nanomaterial.

1. INTRODUCTION
The nanopore structures have been extensively investigated as the building blocks for various technological applications such as electronics, optoelectronics [1, 2] and sensors [3]. Recently, as an emerging field, NWs have been utilized for energy harvesting devices, for instance, to convert thermal [4], mechanical [5], and solar energy into electricity [6]. On the other hand, the NPL axial and radial junctions provide a three dimensional (3-D) geometric configuration for reduced surface optical reflection and enhanced absorption. The enhanced carrier collection and optical absorption can in principle enable more efficient PVs as compared to planar structures. However, the surface and the interface area enhancement also result in an increase in surface/interfacerecombination events. The ordering of the NPL arrays may be used as light trapping schemes analogous to random surface texturing or periodic grating couplers in thin films [7]. A porous anodization of aluminium oxide (AAO) template is fabricated for subsequent NPL growth at the bottom of each pore. The AAO template is etched back, exposing the pillars, and the semiconductor absorber layer is then deposited. This process enables the fabrication of an NPL cell on a low-cost Al metal foil. When anodized in an acidic environment with proper process conditions, aluminium oxidizes to form a porous alumina layer consisting of hexagonally packed arrays of nanopores [8], the pores are normal to the aluminium surface and extend from the surface to the alumina/aluminium interface where there is an oxide barrier layer with near-hemispherical geometry. The shape and size of the pores are relatively uniform, with the pitch and diameter being directly proportional to the anodization voltage, and the height controlled by the anodization time. Anodized aluminium oxide (AAO) has proven to be a highly versatile material system that has found important applications in photonics, energy devices including super capacitors, filtration and purification and architectural and anticorrosive finishes [9-11]. Furthermore, given the uniformity of size-controlled nanopores, AAO has been widely utilized as a template for ordered synthesis of nanostructured materials, including metallic and semiconductor nanorods [12-13], nanowires [14-16], nanotubes [17] and nanoparticles [18]. Importantly, aluminium anodization, in principle, is a highly scalable process as long as a stable voltage and current density are applied with a constant electrolyte temperature anodization time and composition. The protection or decoration of Al surfaces by anodization has been used commercially since 1923. It is essential to obtain particles or pores with uniform diameter and shapes and, for the purpose of particular applications, to arrange and embed them in asuperstructure.

The various applications of nano structures or pores are: size quantization effects, high number of surface atoms, and special surface states, special optical, electronic, magnetic and chemical properties. Some of the biomedical applications are decontamination and antibacterial agents, slow release drugs, filter in hemodialysis, enzyme mimetics and biosensors and adjuvant in anticancer therapy. Self-organized ‘nanopore’ structures in anodic alumina films, called “alumite”, have attracted great attention due to their high pore density and their potential use for masking or information storage. When the pores are filled with metals or semiconductors in a subsequent alternating-current reductive electrolysis, these films can be fabricated into interesting magnetic recording, electronic, and electro optical devices [17-19]. By considering these constraints, here demonstrated continuous change in pore diameter, wall thickness and inter pore distance as anodization time increases.

Many authors have done their research work in this area; the microscopic image analysis of nanoparticles by edge detection using ant colony optimization has been investigated by Shwetabh Singh [17]. Effect of time on anodized Al₂O₃ nanopore FESEM images using digital image processing techniques was carried out by Parashuram Bannigidad et al. [20]. Size measurement of nanoparticle assembly using multilevel segmented TEM images (FeP) was investigated by Paisarn Muneesawang et. al. [21]. Detecting subsurface circular objects from low contrast noisy images and its applications in microscope image enhancement was carried out by Soham De et al. [22]. A K-means based methodology evaluation of
shape parameters for nano-particles was proposed by Ashish Kumar et al. [23]. Influence of anodizing time on porosity of nanopore structures grown on flexible TLC aluminium films and analysis of images using MATLAB software has been investigated by Vidyasagar et al. [24]. In this paper, the anodic oxide formed on pure aluminium TLC film without any pre-anneal is investigated and the effects of anodizing time, voltage, concentration and temperature on the structural properties of the oxide films are examined in detail through digital image analysis. The FESEM images of Al2O3 films captured at regular intervals of time (A–5 mins, B–9 mins, C–20 mins and D–30 mins) and constant in concentration, temperature and voltage are shown in the Fig.1.

![Fig. 1 FE-SEM images of Al2O3 films captured at regular intervals of time](image)

Automated microscopic image analysis provides an efficient tool for qualitative analysis in modern material science and biological studies. The main advantages of using digital image processing and pattern recognition techniques in conjunction with microscopy for quantitative studies of anodizing alumina; automatic image analysis reduces the amount of tedious work with microscopes needed to perform a more accurate quantitative analysis and these techniques provide an important quantitative tool to analyze the structures and spatial features of Al2O3 films.

2. MATERIALS AND METHODS

TLC Silica Gel 60 F254 plates were procured from Merck. Orthophosphoric acid was procured from s-d fine Chem. Ltd. Mumbai. Double distilled water was used throughout the experiments. DC power supply source measure unit was used as the power supply to measure voltage or current simultaneously (Apha-L6405). MATLAB version 7.9.0.529 (R2009) software, which was installed on PC (hp: G42, 2012) used for image analysis. TLC plates were cut into proper size of 2 x 4 cm (0.5 mm thickness) of the following chemical composition (wt%): Al 99.79% (Aluminium), Cu 0.05% (Copper), Mg 0.05% (Magnesium), Si 0.05% (Silicon), Mn 0.05% (Manganese) and Zn 0.01% (Zinc). Coated silica was removed by rubbing the surface using emery sheet grit 600. The Al plates were washed with distilled water, rinsed with ethanol, degreased with acetone in ultrasonic bath for 15 min. Finally, the Al plates were purged by distilled water in ultrasonic bath for another 10 min. Before anodizing, the electrochemical polishing of samples was carried out in a 0.75M NaOH solution. Al plates were immersed in NaOH solution for 4 min to remove alkaline impurities. The samples were rinsed with distilled water and acetone. Later Al plates were rinsed thoroughly and kept undisturbed in distilled water for 10 min. Anodization was performed in a conventional cell using a platinum helical wire as a cathode. Al was used as the counter-electrode, and typically about 90% of the Al was immersed in the electrolyte while the exposed one was connected to the anode through a crocodile clips. The electrical contact was made at the edge of the electrodes. Pt electrode served as the cathode electrode and the distance from the anode electrode was 3 cm. The samples were anodized in an acidic aqueous solution at different time interval at constant concentration and voltage. Ice cold water was used to maintain low temperatures using thermometer. During anodization the electrolyte was kept undisturbed, and the values of voltage, current, time and temperature were recorded. After the anodization process, the samples were rinsed thrice in deionized water and acetone and dried at 90 °C for 1 hour in an oven and was wrapped in aluminium foil. The variation in the time could be attributed to change in the pore size and wall thickness of the anodized Al2O3 thin films.

3. PROPOSED METHOD

The objective of the present study is to develop an automatic tool to determine the effect of time on nanopore structures formed via electrochemical anodization of high purity Al2O3 films in digital microscopic (Field Emission Scanning Electron Microscope (FESEM) nanopore images. The geometrical and statistical shape features tend to vary with the different anodization parameters, namely, concentration (%), time (min), temperature (°C) and voltage (V). In this paper, an automated method is proposed to depict the effect of time on nanopore structures formed via electrochemical anodization of high purity Al2O3 films indigital microscopic nanopore images.

The geometric shape features: length, width, area and nanopore diameter of Al2O3 nanopore images are defined as below:

**Length**: The longer side of smallest circumscribed rectangle.

**Width**: The shorter side of smallest circumscribed rectangle.

**Area**: The number of pixels belonging to the object provides a measure of the object size.

**Nanopore diameter (Dp)**: The average ratio of major axis and minor axis.

**Interpore Distance (Dn)**: The average ratio of neighboring nanopore centroid distance.

The flow diagram of the proposed method is depicted in the below Fig 2:
The algorithm for segmentation and feature extraction of nanopore regions of FESEM images is given below:

**Algorithm:** Segmentation and feature extraction of nanopore regions:

1. **Step 1:** Input nanopore FESEM image.
2. **Step 2:** Perform pre-processing operations on input image (image enhancement and morphological operations).
3. **Step 3:** Perform segmentation by applying global thresholding on pre-processed image to obtain binarized image (0 representing background and 1 representing objects) and label the objects.
4. **Step 4:** Compute geometric shape features; length, width, area, pore diameter, interpore distance and wall thickness for each labeled object on step 3.
5. **Step 5:** Repeat the steps 1 - 4 for all objects.
6. **Step 7:** Analyze and interpret the results.

### 4. EXPERIMENTAL RESULTS AND DISCUSSION

The experimentation of the proposed method is carried on Intel(R) Core(TM) Duo T6670 @ 220GHz with 2GB RAM using MATLAB R2010b software. Every Al₂O₃ FESEM image used in the experiment are captured at regular intervals of time (min) keeping concentration (%), temperature (°C) and voltage (V) constant (Fig. 3. (i)). The input images are converted into gray scale image (Fig. 3. (ii)) and morphological operations such as erosion, reconstructions and dilation are applied. Then performed segmentation by applying global thresholding (Fig. 3. (iii)) to separate background and foreground (nanopores). Geometric shape features, i.e., length, width, area, pore diameter and interpore distance was computed for each labelled segment. Finally, the results are interpreted and compared with manual results obtained by the chemical experts and these results are shown in the Table 2. The details of chemical compositions used for preparation of Al₂O₃ nanopores during synthesis are given in the Table 1.

![Flow diagram of proposed method](image)

<table>
<thead>
<tr>
<th>Image</th>
<th>Concentration (%)</th>
<th>Time (min)</th>
<th>Temp (°C)</th>
<th>Velocity (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>5</td>
<td>5</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>B</td>
<td>5</td>
<td>9</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>C</td>
<td>5</td>
<td>20</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>D</td>
<td>5</td>
<td>30</td>
<td>20</td>
<td>50</td>
</tr>
</tbody>
</table>

It is observed that, if the anodization time (min) increases keeping the concentration (%), temperature (°C) and voltage (V) constant, the pore size increases and the wall thickness decreases. The manual results obtained by chemical experts and computed results of time versus wall thickness is depicted in the Fig. 4. Similarly, the results of time versus nanopore size are shown in the Fig. 5. Finally, the effect of anodizing time on wall thickness and pore diameter of the Al₂O₃ films are shown in the Fig. 6.

**Table 2. Geometric feature values of Al₂O₃ nanopore images of Fig. 4**

<table>
<thead>
<tr>
<th>Image</th>
<th>Wall Thickness (nm)</th>
<th>Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>58</td>
<td>58</td>
</tr>
<tr>
<td>B</td>
<td>56</td>
<td>57</td>
</tr>
<tr>
<td>C</td>
<td>48</td>
<td>49</td>
</tr>
<tr>
<td>D</td>
<td>26</td>
<td>41</td>
</tr>
</tbody>
</table>
5. CONCLUSION

In this paper, an automated method is proposed to measure the effect of anodization time on nanopore structures formed via electrochemical anodization of high purity Al₂O₃ films in digital microscopic nanopore images. The geometric shape features like length, width, area, and interpore distance are extracted and computed. It is found that the structure and regularity of nanopores arrangement is significantly improved by increasing anodizing time (min) at constant concentration (%), temperature (°C) and voltage (V). It is also observed that, after the anodizing process at every interval of time there is a significant decrease in wall thickness from 58 nm to 41 nm and increase in nanopore size from 32 nm to 78 nm. The experimental results are compared with the manual results obtained by the chemical expert and demonstrate the efficiency of the proposed method. The future scope of the research is to compute porosity and design fuzzy inference rules to predict the wall thickness and pore size for various time intervals at constant concentration, temperature and voltage.

6. REFERENCES


