Measurement of Physical Properties of Anodized Al_2O_3 FESEM Images

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ABSTRACT
The objective of the proposedstudy is to develop an automated tool to determine the effect of time onnanopore structures. The designed tool extracts the nanopores from the Al_2O_3 FESEM images and computes their geometrical and statistical features. These valuesare further used to measure the variance of wall thickness and nanopore size which depend on four prominent anodizing parameters, namely, concentration (%), time (min), temperature (^oC) 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 (^oC) 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 58nm to 41nm and increase in nanoporesize from 32nm 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, Al_2O_3, Nanotechnology.

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

1. INTRODUCTION
The nanopore structures havebeen extensively investigated as the building blocks forvarious technological applications such as electronics, optoelectronics [1, 2] and sensors [3]. Recently, as an emerging field, NWs have been utilized for energy harvestingdevices, for instance, to convert thermal [4], mechanical [5],and solar energy into electricity [6]. On the other hand, theNPL axial and radial junctions provide a three dimensional (3-D) geometric configuration for reduced surface opticalreflection and enhanced absorption. The enhanced carriercollection and optical absorption can in principle enable moreefficient PVs as compared to planar structures. However, thesurface and the interface area enhancement also result in anincrease in surface/interface recombination events. Theordering of the NPL arrays may be used as light trappingschemes analogous to random surface texturization orperiodic grating couplers in thin films [7]. A porousanodization of aluminium oxide (AAO) template is fabricatedfor subsequent NPL growth at the bottom of each pore. TheAAO template is etched back, exposing the pillars, and thesemiconductor absorber layer is then deposited. This processenables the fabrication of an NPL cell on a low-cost Al metalfoil. When anodized in an acidic environment with properprocess conditions, aluminium oxidizes to form a poresalumina layer consisting of hexagonally packed arrays ofnanopores [8], the pores are normal to the aluminium surfaceand extend from the surface to the alumina/aluminiuminterface where there is an oxide barrier layer with nearhemispherical geometry. The shape and size of the pores arerelatively uniform, with the pitch and diameter being directlyproportional to the anodization voltage, and the heightcontrolled by the anodization time. Anodized aluminiumoxide (AAO) has proven to be a highly versatile materialsystem that has found important applications in photonics,energy devices including super capacitors, filtration andpurification and architectural and anticorrosive finishes [9-11]. Furthermore, given the uniformity of size-controllednanopores, AAO has been widely utilized as a template forordered synthesis of nanostructured materials, includingmetallic and semiconductor nanorods [12-13], nanowires [14-16], nanotubes [17] and nanoparticles [18]. Importantly,aluminium anodization, in principle, is a highly scalableprocess as long as a stable voltage and current density areapplied with a constant electrolyte temperature anodizationtime and composition. The protection or decoration of Alsurfaces by anodization has been used commercially since1923.It is essential to obtain particles or pores withuniform diameters and shapes and, for the purpose ofparticular applications, to arrange and embed them in asuperstructure.

The various applications of nano structures or pores are; size quantization effects, high number of surfaceatoms, and special surface states, special optical, electronic,magnetic and chemical properties. Some of the biomedicalapplications are decontamination and antibacterial agents,slow release drugs, filter in hemodialysis, enzyme mimeticsand biosensors and adjuvant in anticancer therapy. Self-organized“nanopore” structures in anodic alumina films,called “alumite”, have attracted great attention due to theirhigh pore density and their potential use for masking orinformation storage. When the pores are filled with metals orsemiconductors in a subsequent alternating-current reductiveelectrolysis, these films can be fabricated into interestingmagnetic recording, electronic, and electro optical devices[17-19]. By considering these constraints, here demonstratedcontinuous change in pore diameter, wall thickness and interpore distance as anodization time increases.

Many authors have done their research work in thisarea; the microscopic image analysis of nanoparticles by edgedetection using ant colony optimization has been investigatedby Shwetabh Singh [17]. Effect of time on anodized Al_2O_3nanopore FESEM images using digital image processingtechniques was carried out by Parashuram Bannigidad et.al.[20]. Size measurement of nanoparticle assembly usingmultilevel segmented TEM images (FePt) was investigated by

Paisarn Muneesawang et. al.[21]. Detecting subsurfacecircular objects from low contrast noisy images and itsapplications in microscope image enhancement was carriedout by Soham De et. al. [22]. A K-means based methodologyfor evaluation of

shape parameters for nano-particles wasproposed by Ashish Kumar et. al. [23]. Influence of anodizingtime on porosity of nanopore structures grown on flexibleTLC aluminium films and analysis of images using MATLABsoftware has been investigated by Vidyasagar et. al. [24].In this paper, the anodic oxide formed on purealuminium TLC film without any pre-anneal is investigatedand the effects of anodizing time, voltage, concentration andtemperature on the structural properties of the oxide films areexamined in detail through digital image analysis. TheFESEM images of Al_2O_3 films captured at regular intervalsof time (A–5 mins, B–9 mins, C–20 mins and D – 30 mins)and constant in concentration, temperature and voltage areshown in the Fig.1.

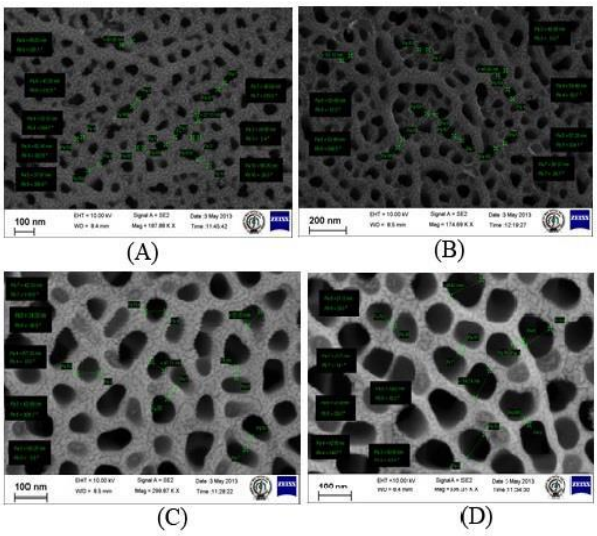

Fig. 1 FE-SEM images of Al_2O_3films captured at regular intervals of time (A–5 mins, B–9 mins, C–20 mins and D–30 mins) and constant in concentration, temperature and voltage

Automated microscopic image analysis provides an efficient tool for qualitative analysis in modern material science and biological studies. The main advantages of using digital imageprocessing 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 animportant quantitative tool to analyze the structures and spatial features of Al_2O_3 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 sourcemeasure unit was used as the power supply to measure voltage or current simultaneously (Aplab: 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 2x4 cm (0.5 mm thickness) of the following chemical composition (wt%): Al 99. 79% (Aluminium), Cu 0.05% (Cupper), 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 Al_2O_3 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 Al_2O_3 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 (^oC) and voltage (V). In this paper, an automated method is proposedto depict the effect of time on nanopore structures formed viaelectrochemical anodization of high purity Al_2O_3 films indigital microscopic nanopore images.

The geometric shape features;length, width, area and nanopore diameter of Al_2O_3 nanoporeimages 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 (D_p): *The average ratio of major axis and minor axis.*

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

The flow diagram of the proposed method is depicted in the below Fig 2:

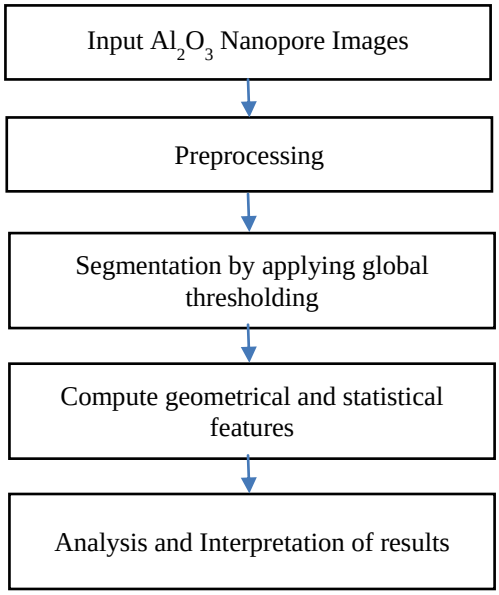

Fig. 2 Flow diagram of proposed method

The algorithm for segmentation and feature extraction of nanopore regions of FESEM images is given below:

Algorithm: Segmentation and feature extraction of nanopore regions:

Step 1: Input nanopore FESEM image.

Step 2: Perform pre-processing operations on input image

(image enhancement and morphologicaloperations).

Step 3: Perform segmentation by applying globalthresholding on pre-processed image to obtainbinarized image (0 representing background and 1representing objects) and label the objects.

Step 4:Compute geometric shape features; length, width, area,porediameter, interpore distanceand wall thickness for each labeled object on step 3.

Step 5:Repeat the steps 1 - 4 for all objects.

Step 7: Analyze and interpret the results.

4. EXPIREMENTAL RESULTS AND DISCUSSION

The experimentation of the proposed method iscarried on Intel(R) Core(TM) Duo T6670 @ 220GHz with 2GB RAM using MATLAB R2010b software. Every Al_2O_3FESEM image used in the experiment are captured at regularintervals of time (min) keeping concentration (%),temperature (^oC) and voltage (V) constant (Fig. 3. (i)). Theinput images are converted into gray scale image (Fig. 3 (ii))and morphological operations such as erosion, reconstructionsand dilation are applied. Then performed segmentation byapplying global thresholding (Fig. 3 (iii)) to separatesbackground and foreground (nanopores). Geometric shapefeatures, i.e., length, width, area, pore diameter and interpore distance was computed for each labelled segment. Finally, theresults are interpreted and compared with manual resultsobtained by the chemical experts and these results are shownin the Table 2. The details of chemical compositions used forpreparation of Al_2O_3 nanopores during synthesis are given inthe Table 1.

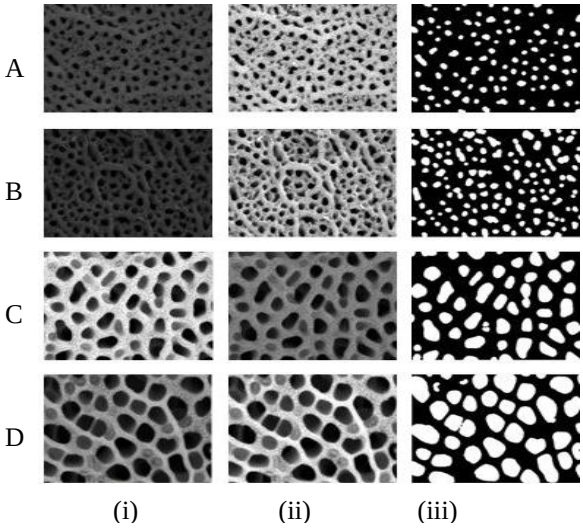

Fig 3: (i) Original FESEM images at different time intervals, (ii) Gray scale images, (iii) Segmented images

Table 1. The details of chemical compositions for preparation of Al_2O_3 nanopore

Image	Concentration (%)	Time (min)	Temp (^oC)	Velocity (V)
A	5	5	20	50
B	5	9	20	50
C	5	20	20	50
D	5	30	20	50

It is observed that, if the anodization time (min) increases keeping the concentration (%), temperature (^oC) 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 porediameter of the Al_2O_3 films are shown in the Fig.6.

Table 2. Geometric feature values of Al_2O_3 nanopore images of Fig. 4

Image	Wall Thickness (nm)		Pore Size (nm)	
	Manual	Proposed	Manual	Proposed
A	58	58	32	32.00
B	56	57	34	34.74
C	48	49	58	61.25
D	26	41	81	78.62

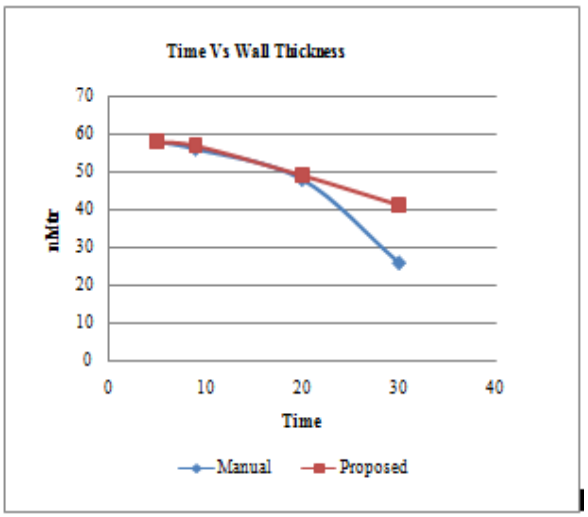

Fig. 4 Time versus nanopore wall thickness of Al_2O_3 image

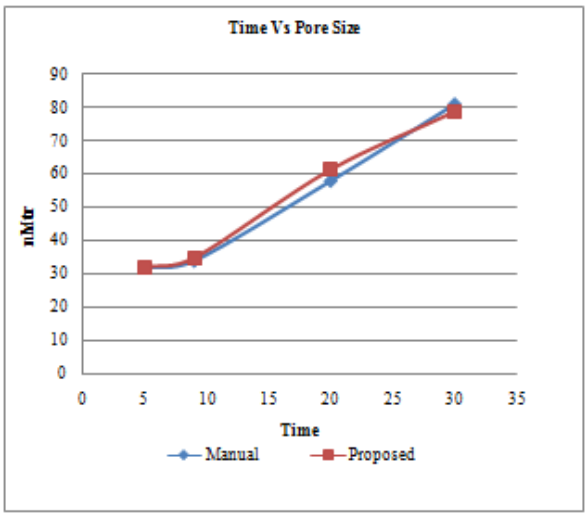

Fig. 5 Time versus nanopore size of Al_2O_3 image

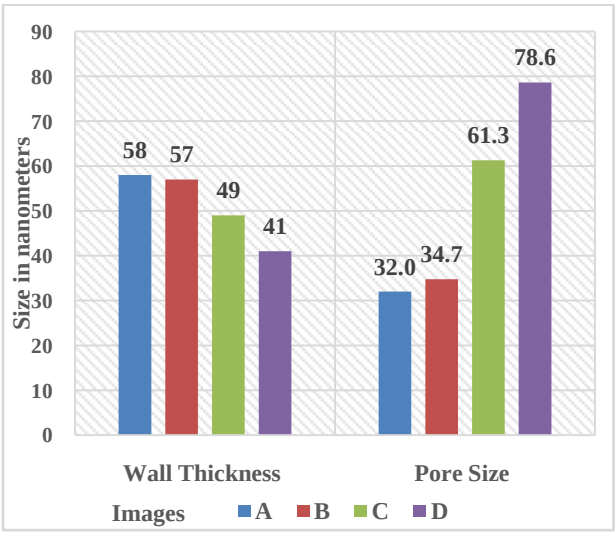

Fig. 6 The effect of anodizing time on wall thickness and nanopore diameter of the Al_2O_3 films

5. CONCLUSION

In this paper, an automated method is proposed to measure the effectof anodization time on nanopore structures formed via electrochemicalanodization of high purity Al_2O_3 films in digital microscopicnanopore images.The geometric shape features like length, width, area, and interpore distance are extracted and computed. It is found that the structure and regularity ofnanopores arrangement is significantly improved byincreasing anodizing time (min) at constant concentration(%), temperature (^oC) and voltage (V). It is also observed that,after the anodizing process at every interval of time there is asignificant decrease in wall thickness from 58nm to 41nm andincrease in nanopore sizefrom 32nm to 78nm. The experimental resultsare compared with the manual results obtained by thechemical expert and demonstrate the efficiency of theproposed 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

[1] Zhong, Z. H., Qian, F., Wang, D. L., Lieber, C. M.Synthesis of P-Type Gallium Nitride Nanowires forElectronic and Photonic Nanodevices. Nano Lett.2003, 3, 343-346.

[2] Qian, F., Gradecak, S., Li, Y., Wen, C. Y., Lieber,C. M. (2005). Core/Multishell NanowireHeterostructures as Multicolor, High-Efficiency Light-Emitting Diodes. Nano Lett. 5, 2287-2291.

[3] Fan, Z. Y., Wang, D. W., Chang, P. C., Tseng, W.Y., Lu, J. G. (2004). ZnO Nanowire Field Effect Transistor And Oxygen Sensing Property. Appl. Phys.Lett. 85, 5923-5937.

[4] Hochbaum, A. I., Chen, R. K., Delgado, R. D.,Liang, E. C., Garnett, W. J., Najarian, M.,Majumdar, A., Yang, P. D. (2008). EnhancedThermoelectric Performance Of Rough Siliconnanowires. Nature, 451, 163-167.

[5] Wang, Z. L., Song, J. H. (2006). PiezoelectricNanogenerators Based On Zinc Oxide NanowireArrays. Science, 312, 242-246.

[6] Fan, Z. Y., Razavi, H., Do, J. W., Moriwaki, A.,Ergen, O., Chueh, Y. L., Leu, P. W., Ho, J. C.,Takahashi, T., Reichertz, L. A., Neale, S., Yu, K.,Wu, M., Ager, J. W., Javey, A. (2009). Three-Dimensional Nanopillar-Array Photovoltaics On Low-Cost And Flexible Substrates. Nature Mater. 8, 648-653.

[7] Stiebig, H., Senoussaoui, N., Zahren, C., Haase, C.,Muller, J. Prog. (2006). Silicon Thin-Film Solar CellsWith Rectangular-Shaped Grating Couplers.Photovoltaics, 14, 13-24.

[8] Masuda, H., Fukuda, K. (1995). Ordered MetalNanohole Arrays Made by a Two-Step Replication of Honeycomb Structures of Anodic Alumina. Science,268, 1466-1468.

[9] Banerjee, P., Perez, I., Henn-Lecordier, L., Lee, S.B., Rubloff, G. W. (2009). Nanotubular metalinsulator-metal capacitor arrays for energy storage.Nat. Nanotechnol. 4, 292-296.

[10] Liang, Y., Schwab, M. G., Zhi, L., Mugnaioli, E.,Kolb, U., Feng, X., Meullen, K. J. (2010). DirectAccess to Metal or Metal Oxide Nanocrystals Integrated with One-

dimensional Nanoporous Carbonsfor Electrochemical Energy Storage. Am. Chem. Soc.132, 15030-15037.

[11] Min Hyung, L., Namsoo, L., Daniel Ruebusch, J.,Jamshidi, A., Kapadia, R., Lee, R., Joon Seok, T.,Takei, K., Young Cho, K., Fan, Z., Jang, H., Wu, M.,

Cho, G., Javey, A. (2011). Roll-to-Roll Anodizationand Etching of Aluminum Foils for High-ThroughputSurface Nanotexturing. Nano Lett. 11, 3425-3430.

[12] Kumar, G., Tang, H. X., Schroers, J. (2009).Nanomoulding with Amorphous Metals Nature, 457, 868-872.

[13] Lyvers, D. P., Moon, J. M., Kildishev, A. V., Shalaev, V. M., Wei, A. (2008). Gold NanorodArrays as Plasmonic Cavity Resonators. ACSNano, 2, 2569.

[14] Vlassiouk, I., Krasnoslobodtsev, A., Smirnov, S.,Germann, M. (2008). Direct detection and separationof DNA using nanoporous alumina filters. Langmuir, 2004, 20, 9913-9915.

[15] Diggle, J. W., Downie, T. C., Goulding, C. W. (1969). Anodic oxide films on aluminum Chem. Rev. 69, 365-405.

[16] Feiyue, L., Zhang, R., Metzger, M . (1998). On the Growth of Highly Ordered Pores in Anodized Aluminum Oxide. Chem. Mater. 10, 2470-2480.

[17] Shwetabh, S. (2013). Microscopic Image Analysis ofNanoparticles by Edge Detection Using and Colony Optimization. J. Computer Eng. 11, 84-89.

[18] Fisker, R., Carstensen, J. M., Hanshen, M. F.,Bodker, F., Morup, S. (2000). Estimation of nanoparticle size distributions by image analysis. J. Nanoparticle Res. 2, 267-277.

[19] Rafael, C. G., Richard, E. W. (2002). Digital Image

Processing; Pearson Education Asia

[20] Parashuram Bannigidad, C. C. Vidyasagar (2015), Effectof Time on Anodized Al_2O_3 Nanopore FESEM Imagesusing Digital Image Processing Techniques: A Study onComputational Chemistry IJETTCS, ISSN 2278-6856,4, 3, 15-22.

[21] Paisarn Muneesawang, Chitnarong Sirisathitkul (2015)Size Measurement of Nanoparticle Assembly UsingMultilevel Segmented TEM Images, Journal onNanomaterials, Hindawi Publishing Corporation, Article

ID 790508, 8.

[22] Soham De, Nupur Biswas, Abhijit Sanyal, Pulak Ray andAlokmay Datta (2012) Detecting Subsurface CircularObjects from Low Contrast Noisy Images: Applicationsin Microscope Image Enhancement, IJCEACIE, 6, 7.

[23] Ashish Kumar, Priyadarshni, Preeti Kaushik (2014) A KmeansBased Methodology for Evaluation of shapeparameters for nano-particles, IJARCSSE, 4, 1.

[24] C. C. Vidyasagar, ParashuramBannigidad, H. B.Muralidhara (2016) Influence of anodizing time onporosity of nanopore structures grown on flexible TLCaluminium films and analysis of images using MATLAB software, Adv. Mater. Lett. VBRI Press, 7(1), 71-77.