

# SYNTHESIS OF AAO MEMBRANES WITH DIFFERENT PATTERNS AS TEMPLATE FOR NANOMATERIALS PRODUCTION

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## ABSTRACT

Various nanoporous AAO membrane has been obtained by applying different voltages at different temperatures in different electrolytic concentrations with various speeds of rotation. SEM analysis performed for evaluation of results. The best result is obtained at 39V and the temperature of  $-6^{\circ}\text{C}$  with 10wt%  $\text{H}_2\text{SO}_4$  as electrolyte. The temperature influence and effect of speed of rotation of electrolyte for this has been observed.

**Key Words:** AAO Membrane, Electrolyte Temperature, Speed Of Rotation Of Electrolyte, SEM Image, Nanopores Array.

## I. INTRODUCTION

Nowadays, one-dimensional (1-D) nanomaterials (nanorods, nanowires, nanobelts and nanotubes) have been attractive due to their physical and chemical properties. These nanostructures in particular show results in electronics magnetic, optics, etc., that have great potential applications in the next generation of nanodevices. Various methods such as chemical vapor deposition (CVD), laser ablation, thermal evaporation, hydrothermal process, and anodic aluminum oxide (AAO) membrane assisted synthesis method have been employed to prepare 1-D nanomaterials. AAO membrane-based assembling has been widely applied in recent years to produce nanowires with extremely long length and high aspect ratios, and it also provides a simple, rapid and cheap way for fabricating nanowires as aligned arrays.

Nanosize templates are a very interesting and promising alternative to grow nanomaterials or to transfer nanosize patterns onto a substrate without the need for complex and costly nanolithographic techniques. Moreover if successfully filled with ferro-electric materials these templates can be used to realize large arrays of nanocapacitors for Fe-RAM. Nanofabrication by self-organization methods has attracted much attention owing to the fact that it enables mass production without the use of expensive lithographical tools, such as an electron beam exposure system. Among the nanosize templates anodic aluminum oxide (AAO) templates have attracted quite some attention because of the highly regular structures and high pore density that can be achieved. AAO templates are suitable for many technical applications, such as the nanopatterning of Si substrate, the fabrication of highly ordered metallic nanowire arrays, the growth of carbon nanotubes or the realization of nanocapacitors arrays.

The area of electrochemistry is another exciting application of template synthesis. Among the various methods that can be used to obtain nanoarrays, template synthesis using electro-deposition has shown to be a low cost and high yield technique for producing arrays of nanowires. The structure of AAO, which has been found to be stable at high temperature and in organic solvents, and exhibits pores uniform, parallel and perpendicular to the surface, is considered the ideal deposition template, so that highly ordered hexagonal arrays of parallel metallic nanowires (Cu, Ni, Bi, Au, Ag) can be synthesized by electro-deposition.

Therefore in these days template synthesis of nanomaterial particularly using anodized aluminium oxide membranes has been developed. Controlled anodization of aluminium in aqueous acids has been applied to synthesis of a nm-scale porous structure with closed packed cells.

The appearance of pores during anodization depends on the oxidation rate of aluminium which is directly controlled by electrolyte temperature and applied voltage.

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In the first case, the template of AAO can be used as a mask for the fabrication of a huge variety of nano-devices the aim is transferring the hexagonal array of cells directly into the underlying Si substrate, without the need for an alumina film transfer. The area of electrochemistry is another exciting application of template synthesis. Among the various methods that can be used to obtain nanoarrays, template synthesis using electrodeposition has shown to be a low cost and high yield technique for producing arrays of nanowires.

Recently, the growth of carbon nanotubes (CNTs) on AAO has been intensively investigated. The particular characteristics of the AAO templates, such as controllable pore diameter and periodicity, narrow distribution of pore size and the pore ideal cylindrical shape, offer the possibility to control the size and the shape of CNT grown out of the pores [5-6].

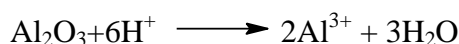
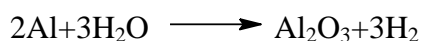
As an alternative processing route developed a nano-indentation technique leading to a pre-texturing of aluminium by imparting with SiC mold is given by Masuda et al [7-10].

In the present paper the anodization of aluminium in sulphuric acid solution is described.

The two step anodizing process produced some pattern of pores on aluminium surface.

## II. MATERIALS AND METHOD

The following chemical reactions involved in the anodization process:



The simple electrochemical cell with power full chiller is employed for anodization.

Pre anodization treatment is given to aluminium foil (3cm X 3cm coupons) (Obtained from Alfa Aesar) of .25mm thickness firstly by annealing at 430°C after treating the surface with 10wt% NaOH solution followed by degreasing with acetone in ultrasonic bath. Electroplating of foil has achieved in 1:3 molar ratio of HClO<sub>4</sub> and

$C_2H_5OH$  at  $6^{\circ}C$  by applying current density  $50mAcm^{-2}$ . The back surface area and edges of the sample were insulated by an acid resistant paint layer.

Two step anodizing processes are employed at a cell potential of 15V, 25V, 39V in 10wt %  $H_2SO_4$  at 6, 0 and  $-6^{\circ}C$  temperature. In first step after 15 minutes of anodization, the aluminium oxide formed was removed by chemical etching in a mixture of 6 wt% of  $H_3PO_4$  and 1.8 wt % of  $H_2CrO_4$  at  $75^{\circ}C$ . After this aluminum foil was re-anodized under same conditions for 9 hrs. During anodization stirring of electrolyte is achieved by using magnetic stirrer at different speeds i.e at 1000, 1500 and 2000rpm thus removing heat of anodization. After anodization the samples were etched with saturated  $HgCl_2$  solution for the removal of remaining aluminum. This was followed by the treatment of 5% phosphoric acid to the samples as it is necessary for the pore opening process. AAO membrane formed shown in fig.1 After anodizing, the ordering of the pores on the top of the aluminium foils were investigated by scanning electron microscope (SEM Model: - HITACHI-6100) at Punjab Agricultural University, Ludhiana (Punjab,India).

### III. RESULT AND DISCUSSION

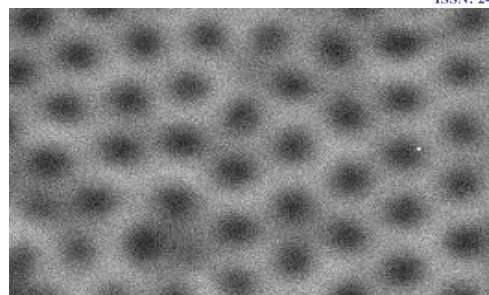
The pores formed on the surface of aluminium are seen (Fig.2-4). The pores formed at  $6^{\circ}C$  and potential difference of 15 volt and at a speed of stirring of electrolyte of 1500rpm are more regular than pores formed at 25V at same temperature with a speed of 1000rpm. Defects in the hexagonal arrangement of pores are there particularly at the boundaries between domains. The geometry of the pores was different when same potential difference was applied at  $0^{\circ}C$  with a speed of 1500rpm. Potential difference of 39V gave better uniformity of pores than 25V at a speed of 2000rpm. Here suggested that decrease in temperature of electrolyte which was obtained by combined effect of Chiller and speed of electrolyte results in the some what restricted movement of ions thus controlling the pore formation. Hence at low temperature the regularity of nanopores arrangement can be increased by applying high anodizing potential [10].

The anodization at  $-6^{\circ}C$  by applying 39V at a speed of 2000rpm resulted in the maximum uniformity in the arrangement of pores, while at 15V and speed of 1500rpm the arrangement of pores was random as compared to 25V and speed of 1500rpm. This further supports that the high anodizing potential at low temperature with maximum speed of stirring results in regularity of pore. The pore diameter increases with decreasing temperature of electrolyte this fact is cleared from SEM images.

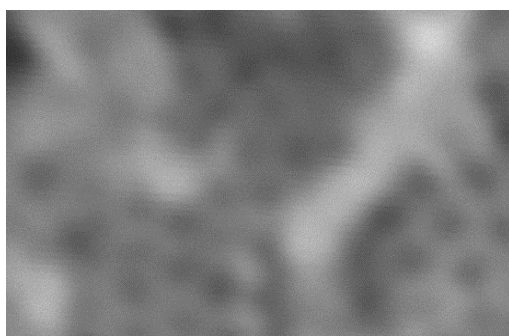
The effective growth rate of oxide layer were calculated from the thickness of oxide layer estimated from SEM on samples treated by two step anodization process. The effective growth of the oxide layer on anodized aluminium achieved in our experimental condition at 39V. The etching time after first step has also pronounced effect on the formation and arrangement of pores. Etching for more than 4 minutes results in the pits and cracks on the metal surface and no porous structure could be obtained.



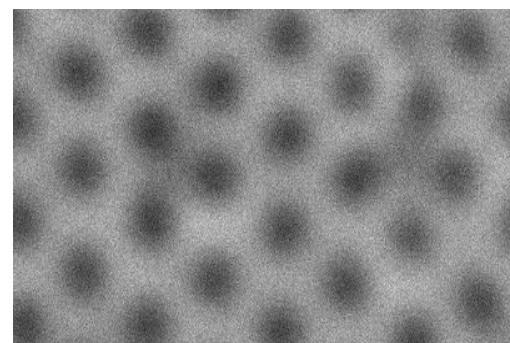
**Fig.1 Photograph of AAO membrane**



**Fig.2 SEM Image of AAO membrane at 15V , 6<sup>0</sup>C and 1500rpm**



**Fig.3 SEM Image of AAO membrane at 25V , 0<sup>0</sup>C and 1500rpm**



**Fig.4 SEM Image of AAO membrane at 39V , -6<sup>0</sup>C and 2000rpm**

#### **IV. CONCLUSION**

It is clearly shown the influence of electrolyte temperature and speed of stirring of electrolyte on the pattern of pores formation on the surface of aluminium. It was found that regularity of pores increases at low temperature (below 0<sup>0</sup>C) and high speed of stirring of electrolyte by applying voltage (25-39V DC). In the range of potentials, electrolyte temperatures and speed of stirring the best hexagonal arrangement found at 36V , -6<sup>0</sup>C and 2000rpm.

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