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Template Formation By Aluminium Anodization Processes For The Synthesis Of Nanomaterials

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Abstract

Various nanoporous AAO membrane has been obtained by applying different voltages at different temperatures in different electrolytic concentrations. SEM analysis performed for evaluation of results. The best result is obtained at 30V and the temperature of -7 ^{0}C with 20 wt% H_2SO_4 as electrolyte. The temperature influence for this has been observed.

Keywords : SEM, temperature, electrolyte

Introduction

Nano technology is sweeping through all fields of science and engineering. Public is becoming aware of the quote of Richard Smalley -Nobel laureate; "Just wait as - the next century is going to be incredible. We are about to be able to build things that work on the smallest possible length scales, atom by atom. These little nano things will revolutionize our industries and our lives ." Nano science & technology will change the nature of almost every human made object in next few years.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.

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 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[1-4].

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. 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 electrodeposition.

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.

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Materials and Method

The following chemical reactions involved in the anodization process:

$2Al+3H_2O \rightarrow Al_2O_3+3H_2$

$Al_2O_3+6H+ \rightarrow 2Al_3++3H_2O$

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 0.25mm thickness firstly by annealing at 50 °C after treating the surface with 10 wt% NaOH solution followed by degreasing with acetone in ultrasonic bath. Electroplating of foil has achieved in 1:3 molar ratio of $HClO_4$ and C_2H_5OH at 7 °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 18V, 20V, 30V in 20wt % H_2SO_4 at 5, 0 and -7 °C temperature. In first step after 20 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 70°C. After this aluminum foil was re-anodized under same conditions for 12 hrs. During anodization continuous stirring of electrolyte is achieved by using magnetic stirrer (1500 rpm) 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).

Result and Discussion

The pores formed on the surface of aluminium are seen (Fig.2-4). The pores formed at 5 °C and potential difference of 18 volt are more regular than pores formed at 20V at same temperature. 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 °C. Potential difference of 30V gave better uniformity of pores then 20V. Here suggested that decrease in temperature 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 by anodization at -7 °C [10]. The anodization at -5 °C by applying 30V resulted in the maximum uniformity in the arrangement of pores, while at 18V the arrangement of pores was random as compared to 20V. This further supports that the high anodizing potential at low temperature results in regularity of pore. The pore diameter increases with increasing 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 30V. The etching time after first step has also pronounced effect on the formation and arrangement of pores. Etching for more then 5 minutes results in the pits and cracks on the metal surface and no porous structure could be obtained.

Figure 1. Photograph of AAO membrane

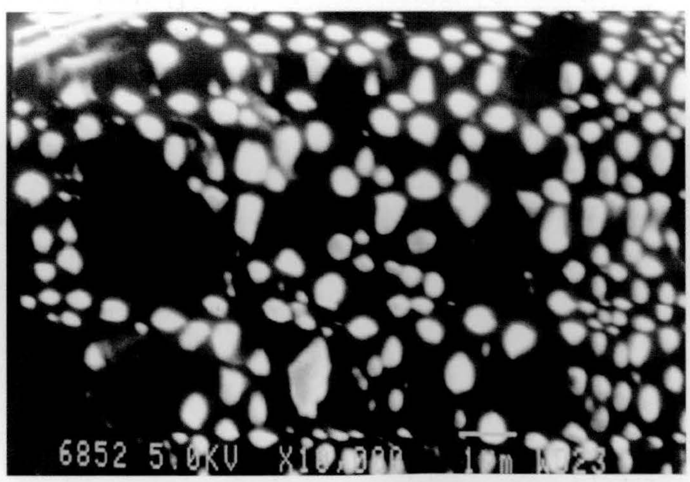

Figure 2. SEM Image of AAO membrane at 18V and 5°C

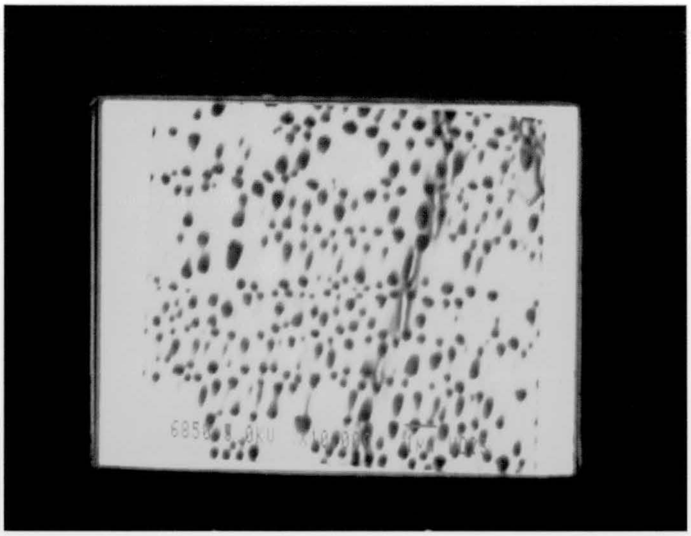

Figure 3. SEM Image of AAO membrane at 20V and 5°C

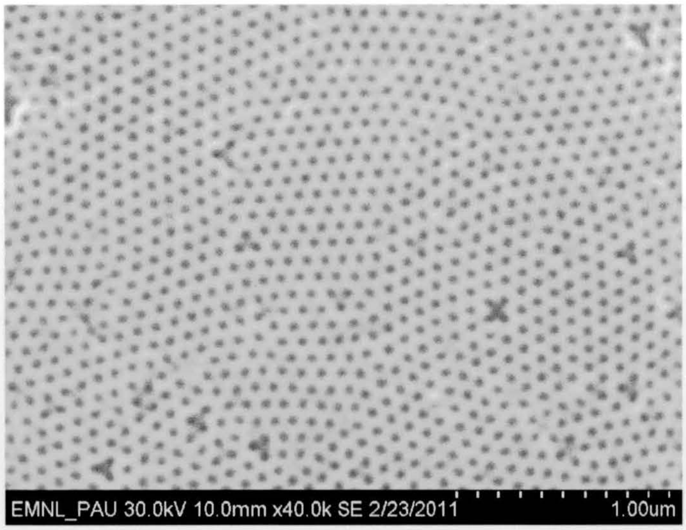

Figure 4. SEM Image of AAO membrane at 30V and -7°C

Conclusion

It is clearly shown the influence of electrolyte temperature on the pattern of pores formation on the surface of aluminium. It was found that regularity of pores increases at low temperature (below 0 °C) of electrolyte by applying high voltage (20-30V DC). In the range of potentials and electrolyte temperatures the best hexagonal arrangement we have found at 30V at -7 °C .

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