ABSTRACT

Foil-based Anodized Aluminum Oxide (AAO) templates, with pore diameters 22-28nm, were successfully synthesized using simple hard anodization techniques with 10% Sulphuric acid as the electrolyte. Pore widening and anodization conditions were also optimized to 25min using 6% Phosphoric acid and using external potential of 15V, without destroying the overall structural integrity of the template. An alternative barrier layer perforation technique by reverse biasing of the Aluminum foil was also investigated and found to be ineffective in removing the barrier layer. Glass, Silicon and ITO based AAO, with pore diameter of 20nm, were also successfully synthesized with high degree of consistency and pore diameter of 20nm. RF- Sputtering conditions of Al target were also optimized to 100W, 10.0mTorr with 10 cycles of 900s produced thickness of 300nm. Electrodeposition of Ni nanowires using these extremely small pore templates were unsuccessful, with metallic Ni being deposited on the top of the template. Synthesis of multi-layered core-shell nanowires via simple metal displacement reaction between Ni and Cu was also investigated using commercially available AAO. Surface topography of all samples was characterized using Scanning Electron Microscope (SEM) and elemental analysis of deposition of Ni and Cu were conducted using Electron Diffraction X-ray (EDX).

INTRODUCTION

The one-dimensional (1D) system is a very exciting entrant from a fundamental and application viewpoint. Numerous applications from nano-sized scaled structures require well-defined free standing 1D nanostructure. One such synthesis technique was the use of anodic aluminum for template assisted synthesis of metallic nanowires. Synthesis of highly ordered anodized aluminum oxide (AAO) templates was first reported by H. Masuda and K. Fukuda in 1995 using a two step anodization process. Synthesis of AAO on various substrates such as Silicon wafers and Glass had also been reported elsewhere with extensive work published by Xu et al. However, in these reports, AAO synthesized had large pore diameter size of 80-200nm, and the authors used rather powerful techniques such as Reactive Ion Etching. In fact, AAO with pore diameter of 100-200nm are commercially available. Therefore, the task at hand was to optimize the synthesis of foil and substrate based AAO and achieve pore diameter less than 50nm and also to check the viability for the use of these AAO in growing of metallic nanowires. This project aims to study and optimize the synthesis of AAO arrays on various substrates, and to refine these techniques in search of a better
modus operandi for the synthesis of single layer nanowires as well as multi-layered core-shelled nanowires, using simple electrodeposition techniques.

**Procedure**

**Part A: General Synthesis of Foil-based AAO and Optimization of Synthesis**

Al foil, 99.999% purity was annealed. The foil was then pretreated in acidic and alkaline mixtures and anodized at 18V, 0 °C using a two-step anodization process in 10% H₂SO₄. After which, the Al layer was removed using saturated HgCl₂ solution and AAO was cut into 4 parts and immersed in 6% H₃PO₄ for 20min, 25min, 30min and 35 min. Samples were then characterized using SEM. Investigation of acid etching with Al attached was also carried out. Another foil AAO produced using was subjected to reverse bias etching at -5V at varying duration of 5min, 10min, 15min and 20min in the same electrolytic solution along with acid etching to remove barrier layer. Another foil AAO was produced using a reduced voltage of 15V.

**Part B: General Synthesis of Substrate-based AAO and Optimization of Synthesis**

A comparative study of the surfaces of Sputtered and Electron Beam Evaporated Al with foil Al was carried out. Pt, Cr and Ti (Sputtered and Electron Beam Evaporated) were also investigated as a suitable adhesive layer as well as Au as a conductive layer. The use of oxalic acid against sulphuric acid as electrolyte was also conducted. Optimization of Al layer was also conducted by varying sputtering conditions.

**Part C: Electrodeposition of Nanowires**

Electrodeposition of Ni was conducted on the commercially available AAO as well as synthesized AAO. Electrodeposition of Co nanowires was also conducted as well. Investigation of growing Ni nanowires using Indium Tin Oxide (ITO)-based AAO was also conducted, by first sputtering Al on ITO, and anodization then electrodeposition.

**Part D: Investigation of Multi layer Core shell Nanowire Synthesis using Commercial AAO**

Commercially available AAO was electrodeposited with Ni using the same conditions. AAO was subsequently removed using and then immersed in a 125g/L CuSO₄ solution for 12hrs. Substrate was characterized using SEM with Electron Diffraction X-ray.

**RESULTS AND DISCUSSION**

**Part A: General Synthesis of Foil-based AAO and Optimization of Synthesis**

![Figure 1a-c (left to right): SEM image of Top, Bottom and Side View of 25min acid etching.](image-url)
It was observed that immersion in 6% H$_3$PO$_4$ for 25min was sufficient to remove the incumbent barrier layer as well as maintaining its overall structural integrity. From the measurements, the pore channels had diameter of (28.33 ± 1.78) nm at the top and (27.56 ± 2.09) nm at the bottom.

![Figure 2a and 2b: Side and Bottom view of AAO subjected to 5min Reverse Bias Etching.](image)

From Fig 2b, the honey-combed like structure of the AAO could be observed clearly. However, the method of reverse biasing the AAO for 5min was insufficient to penetrate the barrier layer. The reverse biasing (RB) of the anode to the cathode also created a void layer between the AAO and the Al layer, separating the AAO slightly from the Al layer as shown. Effect of prolonged RB and acid etching destroys the structural integrity of the AAO. Investigation of using a reduced voltage of 15V during anodization yields successfully yields a much smaller pore diameter of (19.02 ± 1.49) nm at the top of the AAO and (21.27 ± 2.38) nm at the AAO bottom respectively. A lowered 15V potential was used as a modus operandi for future anodization instead of the conventional 18V.

**Part B: General Synthesis of Substrate-based AAO and Optimization of Synthesis**

![Figure 3a-c (left to right): SEM (top view) of Al deposited by Electron Beam Evaporator on glass, Al deposited by RF-sputtering, and Al foil annealed and pretreated with acids and alkali.](image)

From Fig 3c, the surface of foil-based AAO had a very rough topography. Comparatively, using the EBE and sputtering machine to deposit Al on glass creates a much smoother surface as shown above. Furthermore, sputtered Al had a better surface than EBE deposited Al. Thus it would be preferred to use sputtered Al than EBE Al or foil Al. Sputtering conditions were also optimized at 100W, 10.0mTorr and 10cycles of 900s produced 300nm thick Al layer.

![Figure 4a (left) and 4b (right): SEM (side view and top view) of AAO on Ti on Si](image)
Anodization was successfully carried out and achieved an average pore size of $(23.00 \pm 4.26)$ nm. Anodization using oxalic acid was also found to be unsuitable, due to high voltage which caused technical difficulties as well as a short shelf life of 1 week. AAO produced by oxalic acid anodization had the same pore diameter as those synthesized by sulphuric acid.

**Part C: Electrodeposition of Nanowires**

![ SEM images of Ni and Co grown on AAO on B-doped Si and ITO-based AAO.](image)

From the SEM images, it was observed that the both Ni and Co were deposited on the top of the AAO rather than into the pores of the template. Higher magnification SEM of the samples showed that the AAO pores were synthesized successfully, with average pore diameter of $(21.62 \pm 1.45)$ nm, but the metal deposition did not occur as expected. Similar results were found using ITO-based AAO which had an even smaller pore diameter of $(18.33 \pm 3.35)$ nm.

**Part D: Investigation of Multi layer Core shell Nanowire Synthesis using Commercial AAO**

Results from the EDX revealed significant Ni peaks but there were no Cu peaks. This meant that displacement reaction was not successful and Cu did not coat the surface of the Ni nanowires. Although the displacement reaction was thermodynamically feasible, the reaction might not be kinetically favorable. The displacement itself might have a significantly high activation energy barrier such that the reaction might not take place under room temperature.

**CONCLUSION AND SUGGESTIONS FOR FURTHER WORK**

Foil-based AAO and substrate-based AAO, with pore diameters of 20-30nm has been successfully synthesized. Conditions for their synthesis had been optimized. However, disappointingly, the use of substrate-based AAO for growing Ni and Co nanowires via electrodeposition method was not successful. It was experimentally discovered that the metals deposited on the top of the AAO rather than into the pores of the template. Perhaps rather than electrodeposition, the templates could be used for other techniques such as sol-gel synthesis of SiOx. Further research of using ITO-based AAO for electrodeposition of Ni is also required. Synthesis of multilayered core shell nanowire synthesis using simple displacement reaction was found to be unsuccessful. Further improvements and optimization is required for this synthesis reaction.
REFERENCES


