Modulated nanopores using pulse anodization on thin aluminum

Mahesh Babu Gunukula
MODULATED NANOPORES USING PULSE ANODIZATION
ON THIN FILM ALUMINUM

by

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ABSTRACT

Modulated Nanopores Using Pulse Anodization on Thin Film Aluminum

by

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Nanoporous anodic aluminum oxide has traditionally been made in one of two ways: “Mild Anodization (MA)” or “Hard Anodization (HA)”. The former method produces self-ordered pore structures but it is slow and only works for a narrow range of processing conditions; the latter method, which is widely used in the aluminum industry, is faster but it produces films with disordered pore structures. Here we report a novel approach termed “pulse anodization” that combines the advantages of the MA and HA processes. By designing the pulse sequences it is possible to control both the composition and pore structure of the anodic aluminum oxide films while maintaining high throughput.
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CHAPTER 1

INTRODUCTION

Nanoporous anodic aluminum oxide (AAO) with self-organized hexagonal arrays of uniform parallel nanopores has been used for various applications in the fields of sensing, storage, separation, and the synthesis of one-dimensional nanostructures. Previously, self-ordered AAOs have been obtained by mild anodization (MA) within limited processing windows (that is, self-ordering regimes). The accessible pore diameters (D_p) and interpore distances (D_{int}) are limited by the self-ordering requirement. However, MA is slow, and it takes more than two days of processing time to obtain nanoporous AAOs that are suitable for applications, so hard anodization (HA) of aluminum, a faster process that was invented in the early 1960s, in an attractive alternative. Classical HA is carried out at relatively low temperatures and high current densities (j>50mA cm^{-2}) by using sulphuric acid (H_2SO_4), and has routinely been used in the aluminum industry to produce anodic films of high technical quality at an efficient rate of production (typically, 50-100 umh^{-1}). However, the pores of the resulting anodic films are less ordered than those produced by MA processes. This has prevented the direct implementation of classical HA processes into current nanotechnology research.

Recently, the fabrication of self-ordered AAO was demonstrated under high anodization potentials and current densities (up to 70V and 200 mAcm^{-2}, respectively)
using an aged sulphuric acid solution, far outside the MA regime (H$_2$SO$_4$: 25V and 2^{-4} mAcem$^{-2}$) but similar to the anodization conditions for HA. Unfortunately, the resulting AAOs were mechanically unstable, with a strong tendency towards crack development under the influence of even weak mechanical forces. More recently our group developed an H$_2$C$_2$O$_4$-based HA, which enabled between 25 and 30 times faster growth (compared to MA) of long-range ordered and mechanically robust AAOs in a self-ordering regime characterized by D$_{nt}$= 200-300nm. It was found that the current density (that is, the electric field strength $E$ at the pore bottom) is an important parameter governing not only the structural parameters of AAO (D$_{nt}$, porosity and thickness of the barrier layer), but also the self-organization of the oxide nanopores for a given anodization potential UHA. Based on these observations, the fabrication of novel AAO membranes with periodically modulated diameters of nanopores was realized, demonstrating that the combination of conventional MA and the newly developed HA could offer a new degree of freedom for tailoring the pore structure of AAOs by combining properties from the two anodization processes. However, each modulation step required the exchange of the electrolyte solutions in order to satisfy both MA and HA processing conditions.

Here, we report a novel approach for continuous structural engineering for continuous structural engineering of nanoporous AAO based on pulse anodization of aluminum under a potentiostatic condition using H$_2$SO$_4$. Periodic pulses consisting of a low-potential pulse followed by a high potential pulse were applied to achieve MA and HA conditions, respectively. We show that combining MA and HA conditions by deliberately designing the pulse sequences allows tailoring of the pore structure as well as the chemical composition of the resulting AAO along the pore axes. This enabled us not
only to completely delaminate a single as-prepared anodic film into a stack of well
defined AAO membrane sheets, but also to realize novel three dimensional (3D) porous
architectures that have the potential to be useful for a broad range of nanotechnology
applications.
2.1 Anodization of Aluminum

When aluminum is exposed to atmosphere it forms a very thin layer of oxide (alumina) that adheres strongly to the surface and protects it from future reaction. A thick layer of oxide can be formed by immersing aluminum in an electrolytic solution and passing electric current; this process of oxidizing aluminum electrochemically is called anodization. The anodized aluminum contains a two dimensional hexagonal lacework of cells with uniform tubular pores. The schematic of the top and the cross section of the porous alumina are shown in fig 2.1. The diameter of the pores and the thickness of the alumina depend on the conditions of anodization such as type and pH of the electrolytic solution, anodizing current density and time. The diameter of the pores can vary from 4nm to 200nm, pore length from 10nm to 1000's of nm. Also, the density of these pores can range from $10^9$-$10^{11}$ cm$^{-2}$ ranges. Although the process of anodization has been around for years, the mechanism of pore formation is not fully understood yet. A near perfect, densely packed self organized hexagonal pore structures for a narrow processing parameters have been reported by researchers in the last 20 years. The cause of this self ordering behavior is believed to be mechanical stress which leads to repulsive interaction between neighboring pores as reported by Jessensky.
The process of anodization can be carried out using two different conditions, by applying constant current or by applying constant voltage. An explanation for the various stages during constant current anodization is given here because majority of the experiments in this thesis were carried out using this condition. The easiest way to monitor the anodization process is to measure the voltage time characteristics. A typical curve during the anodization of bulk aluminum is shown in fig 2.2. A thin layer of nonporous alumina (Al₂O₃) is formed during the first 3-5 sec. This is represented by an increase in the voltage that corresponds to an increase in the net resistance. As the
process of anodization continued, an array of pores develops on the surface and they
grow in diameter before reaching the final dimension that is determined by the processing
conditions. This is indicated by the decrease in the potential that is measured. The
potential finally reaches a steady state value when the final diameter is reached. The
diameter of the pores does not increase any further after this and the depth of the pores
increases with continuing anodization. Over the years, anodization of bulk aluminum has
been investigated quite extensively, however such structures are not suitable for practical
device applications because of the thick unreacted bulk aluminum underneath. To
overcome this limitation, the Nanostructures Research Group has developed the
technology for creating a thin film alumina template on an arbitrary substrate.

Pore formation on bulk aluminum

Figure 2.2: Voltage-Time characteristics during anodization of bulk aluminum.
The Voltage-Time characteristic during constant current anodization of an aluminum film deposited on a silicon substrate is shown in fig 2.3. As seen from the figure, the voltage increases rapidly during the first 3-5 sec due to the formation of a nonporous (dense) alumina layer. The voltage then decreases and reaches a steady state value marked by the formation of pores and reaching the final diameter. After this, the pores grow in a direction perpendicular to the surface of the substrate. When the pores reach the silicon surface the voltage level again increases, which is believed to be due the oxidation of the silicon substrate. The pore formation rate can be accurately modeled because the thickness of the film is known and also the total time for anodization can be obtained in the form the voltage time characteristics. As a result, this approach not only finds the control on the pore diameters but also on the depth of the pores.

Pore formation on thin aluminum

![Figure 2.3: Voltage-Time characteristics during anodization of thin aluminum.](image-url)
The periodicity of the pores can be improved by sing two step anodization process. The anodization in the first step is done using a constant voltage method where the aluminum film is anodized to approximately one-third of its thickness. The anodization by constant voltage gives good periodicity of the pores. The alumina film is then etched using a mixture of chromic acid solution and phosphoric acid. This completely removes the alumina layer and leaves behind foot-prints on the aluminum film. The next step of anodization is carried out using constant current; the pores tend to grow only in the areas of already existing foot-prints. The applied current density controls the diameter of the pores. Thus good control on the periodicity and the pore diameter can be obtained by using this technique.

2.2 Device Fabrication

In a typical fabrication procedure, a tantalum film of thickness 200nm is first deposited on a p-si wafer. Next aluminum layer of thickness 700nm is deposited on top of the tantalum film.

![Diagram of the four layered sandwich structure used for anodization.](image)

Figure 2.4: The four layered sandwich structure used for anodization.
The metal depositions in this project were carried out in the Nanotechnology center at University of California, Santa Barbara. The Al/Ta coated wafer was then cut into small pieces of about 1 sq-cm using a diamond scribe to fit inside the sample holder. The sample was then immersed in an electrolyte which is maintained at room temperature. The silicon substrate, which acts as the anode, was connected to the positive terminal of the power supply. A platinum mesh immersed in the electrolyte was used as the cathode. The solution was stirred continuously to prevent heat build up at the aluminum/electrolyte interface during the anodization process.

![Diagram of anodization setup](image)

Figure 2.5: Schematic of a typical anodization set up.

The thin film aluminum wafer is placed at the anode with the top aluminum layer facing the electrolyte. The power supply can be used in both constant current and constant voltage mode.
As explained earlier the pH of the electrolyte plays an important role in the pore geometry. A 2% sulfuric acid solution was used as the electrolyte for the anodization process. This solution was prepared by adding 20 ml of sulfuric acid to 1000 ml of DI water. Anodization can be carried out under constant current and constant voltage conditions. For constant current anodization, the voltage drops across the anode and the cathode is recorded to monitor the anodization process. For constant voltage anodization, the current flowing between the anode and the cathode is recorded to monitor the anodization process.

2.3 Constant Voltage Anodization

The periodicity of pores on the aluminum surface can be improved by using a constant voltage anodization process is monitored using a constant voltage anodization technique.

![Current-Time characteristics](image)

Figure 2.6: Typical Current-Time characteristics obtained during constant voltage anodization (2% sulfuric acid solution, 20 V at room temperature).
In the constant voltage mode the anodization process is monitored using a current-time graph: a typical graph obtained during the experiments is shown in figure 2.6. As discussed in the previous chapter there are three main physical processes occurring during the anodization process, formation of alumina barrier layer, formation of pores and then the propagation of pores.

These processes can be interpreted from the above current-time characteristics. In the initial few seconds (0-5 sec), the alumina barrier layer is formed. At the juncture between the constant current part and the initial decreasing portion of the graph (point a) the pores are created [18]. After point a pores propagate vertically downwards and the resistance is almost constant.

The experimental set-up similar to that used for the constant current anodization with the power supply adjusted to the constant voltage mode. Since the magnitude of current in such experiments is very small, a series resistor is connected in the circuit and the voltage drop across it is used to measure the circuit current.

2.4 Two Step Anodization

A two-step anodization process was proposed by H.Masuda to obtain a periodic arrangement of pores on bulk aluminum. A similar method is used in this thesis to obtain a periodic array of pores on thin film aluminum.

In step 1, a sandwich structure of Al/Si/Ta/Al is anodized in an electrolyte for 100-120 sec. The initial layer of alumina formed at the top is removed by etching in a chromic acid solution at 60c. This leaves behind a periodic array of dimples on the surface of aluminum. This structure is then further anodized (step II) in the same electrolyte under the same conditions for 500 sec. The pores grow along the dimples
created in step 1, resulting in a more regular array of pores on the surface. The pores are then widened in a mixture of phosphoric and chromic acid solution for 3-5 min to remove the barrier layer and other residues from the anodization process.
CHAPTER 3

EXPERIMENTAL SETUP AND PROCEDURE

In this chapter the typical set up and the procedure to conduct the anodization process are discussed. We have a chiller that has to be started some time before the process starts and a double walled glass burb in which the acid solution and the electrodes are placed. A typical set up of the chiller and glass burb are shown in fig 3.1.

Figure 3.1: Set up of Chiller and Glass Burb
Next device that has to be considered is the power supply. It supplies the power to the electrodes. This power supply can be operated in both constant voltage and in constant current condition. The typical set up of the power supply is shown below in fig 3.2.

![Figure 3.2: Set up of Power Supply.](image)

The important device in the process is the data acquisition system. It acquires the raw data from the process and sends it to the processing unit for further analysis. In our experiment keithley Electrometer acts as the data acquisition system. A typical set up of the Keithley electrometer is shown below in fig 3.3.
Next device that has to be considered is the data processing unit. It takes the raw data from the data acquisition system (Keithley electrometer) and sends the data to lab view software to plot the current time characteristics in constant voltage mode or voltage time characteristics in constant current mode. The set up of data processing unit is shown below in fig 3.4.
The last device in the experimental set up is the lab view software. It draws the graphs in various modes. The obtained graphs are further useful for analysis of the pore formation on the sample. The typical result window is shown below in fig 3.5.

![Figure 3.5: Set up of Lab View Software.](image)

3.1 Operational Procedure of Anodization Apparatus:

3.1.1 Constant Current Anodization:

1. Set the Sample – Holder inside the anodization chamber.
2. Connect two red wires [one from Power supply (PS), and other from Keithley Electrometer (KE)] two the anode (Sample holder).
3. Connect two black wires [one from Power supply (PS), and other from Keithley Electrometer (KE)] two the cathode (Pt mesh).
4. Open the program “UNLV2”.
5. Turn SW-1 in PS to extreme right.
6. Turn SW-4 in PS to extreme right.

7. SW-3 & SW-5 should be in OFF condition.

8. Turn on KE.

9. Select the output type as “Constant Current”.

10. Choose the required current or put specific value of current in the box named “Constant Current”.

11. Turn on SW-2 in PS.

12. Click the arrow symbol in the top-right corner of unlv2 window to save the data.

13. Click “Manual ON/OFF key to ON position.

14. Observe the Voltage – Time curve in the screen. (You can also see the voltages in KE as well as in the DC Voltmeter of PS. The current you have set can also be seen in the DC Mill amperes of PS).

15. To stop the process, hit the power button to STOP condition.

16. Turn off SW-2 in PS.

17. Remove the Red wires from the sample holder.

18. Reload new sample.

19. Follow the above steps again.

3.1.2 Constant Voltage Anodization:

1. Set the Sample – Holder inside the anodization chamber.

2. Connect one wire from Power supply (PS) to the Sample Holder. Connect the other one from PS to a 1 Ω resistor (connected by a green wire). Connect the free end of the green wire to the Pt electrode. The Keithley Electrometer (KE) should be connected across the resistor.
3. Open the program “UNLV2”.

4. Turn SW-1 in PS to extreme right.

5. Turn SW-4 in PS to extreme right.

6. SW-3 & SW-5 should be in OFF condition.

7. Turn on KE.

8. Select the output type as “Constant Voltage.

9. Click the arrow symbol in the top-right corner of unlv2 window to save the data.

10. Voltage Selection window will then be activated (Green Box).

11. Choose the required voltage or put specific value of voltage in the specific box.

12. Turn on SW-2 in PS.

13. Click “Manual ON/OFF key to ON position.

14. Observe the Voltage – Time curve in the screen. (You can also see the voltages in KE as well as in the DC Voltmeter of PS. The current you have set can also be seen in the DC Mill amperes of PS).

15. This voltage can be converted to current dividing by the resistance value (here the voltage and current magnitudes are same as 1 Ω resistance is used).

16. To stop the process, hit the power button to STOP condition.

17. Turn off SW-2 in PS.

18. Remove the wire from the sample holder.


20. Follow the above steps again.
CHAPTER 4

EXPERIMENTS AND RESULTS

4.1 I-V Graphs for Modulated Pore Diameters:

This chapter explains the I-V graphs for modulated pore diameter formation. In order to get modulated pores, anodize under two conditions—“mild anodization”, followed by “hard anodization”. Mild anodization is usually performed at lower voltages about 40V for oxalic acid and results in pores with a certain pore size and a certain cell size. In mild anodization, the oxide growth rate is very slow. The other anodization condition is “hard anodization”, where the oxide growth rate is much faster. This type of anodization is usually performed at higher volts e.g. >110V for oxalic acid. This results in formation of pores again with a certain pore size and a certain cell size. One period of the modulated pore diameter consists of a half cycle of mild anodization followed by another half cycle of hard anodization. The parameters—acid concentration and voltage must be selected so that the cell size remains same. Due to the inherent nature of hard anodization, the pore size for hard anodization is smaller than mild anodization resulting in modulated pores. The cell size depends on voltage applied, acid concentration and current density. We started the experiment by performing constant voltage anodization at 0.3M oxalic acid concentration at different values of voltage, as the graphs in Fig 4.1(a) indicates. In fig 4.1(a) the anodization was done at 40V and 0.3M concentration. We waited as long as 200sec, but Ta wasn’t yet touched. We stopped the anodization and
then resumed as in fig 4.1(b) till about 120 sec. So it took as long as 320 sec to oxidize 750nm of Al. Now we next moved to 50V, where it took as much as 450-500 sec to oxidize Al. So this is the mild anodization regime. In fig 3.3, it took about 150 sec, note that the voltage changed from 70 to 50, marginally, but the time to oxidize, drastically fell down to 100 sec range, indicating onset of hard anodization. In fig 4.4, for 90 V, it took just about 30 sec to oxidize. Now, at 110-120V in fig 4.5 and 4.6, the oxidation was almost instant, may be about 5-6sec range. Observe the drastic time scale difference. From 300-500 sec at mild anodization corresponding to 5-6 sec at hard anodization at 110V range. Thus we may assume 40-50V to be “mild anodization range” and “70-110V” to be in hard anodization range. Note that there is a drastic difference in current densities for HA and MA at the same conc. Such a large difference in current density will give different cell sizes and that will destroy modulated pore structure. Based on this rationale, we reduced the acid conc. to 0.1M and performed HA keeping high voltage and attain a comparable current density.

Figure 4.1(a): Current–Time relationship obtained using 0.3 M Oxalic acid with constant voltage 40 V.
Figure 4.1(b): Anodization resumed at constant 40V and 0.3M Oxalic acid.

Figure 4.2: Current–Time relationship obtained using 0.3 M Oxalic acid with constant voltage 50 V.
Figure 4.3: Current–Time relationship obtained using 0.3 M Oxalic acid with constant voltage 70 V.

Figure 4.4: Current–Time relationship obtained using 0.3 M Oxalic acid with constant voltage 90 V.
Figure 4.5: Current–Time relationship obtained using 0.3 M Oxalic acid with constant voltage 110 V.

Figure 4.6: Current–Time relationship obtained using 0.3 M Oxalic acid with constant voltage 120 V.

Graphs 4.7 – 4.10 indicate the 0.1M concentration of Oxalic acid. For 50V the current was about 8mA and for 40V current was about 4mA. We observe from fig 4.9 and 4.10 that between 100-130V ranges we expect about 8-9mA current. Based on this
rationale, parameter chosen was 50V 0.3M for “Mild Anodization” half cycle and 115V 0.1M for “Hard Anodization” half cycle.

Figure 4.7: Current–Time relationship obtained using 0.1 M Oxalic acid with constant voltage 70 V.

Figure 4.8: Current–Time relationship obtained using 0.1 M Oxalic acid with constant voltage 100 V.
Figure 4.9: Current–Time relationship obtained using 0.1 M Oxalic acid with constant voltage 115 V.

Figure 4.10: Current–Time relationship obtained using 0.1 M Oxalic acid with constant voltage 130 V.

For this final sample, refer to fig 4.11(a) and 4.11(b) for the MA and HA half cycle graphs. We prepared another sample with Mild Anodization at 0.3M 40V and
current attained was 3-4mA. At 0.1M, we found at 70-90V range, the current attained is comparable to 3-4mA as shown in fig 4.7.

Final Sample 1

Figure 4.11(a): First half of final sample 1, corresponding to mild anodization at 0.3M/50 V.

Figure 4.11(b): Second half of final sample 1, corresponding to hard anodization at 0.1M/110 V.
Therefore another sample no. 2 was prepared with Mild Anodization cycle parameters as 0.3M-40V and Hard Anodization cycle as 0.1M-70V as well as 0.1M-90V. The graphs for this are in fig 4.12(a) - 4.12(c).

**Final sample 2**

---

**Figure 4.12(a):** First half of final sample 2, corresponding to mild anodization at 0.3M/40V.

**Figure 4.12(b):** Second half of final sample 2, corresponding to hard anodization at 0.1M/70V.
Figure 4.12(c): Second half of final sample 2, corresponding to hard anodization at 0.1M/90V.
CHAPTER 5

SIMULATIONS

The software used for carrying out the simulations is Nanohub. There are various tools in Nanohub used for simulating the particles at the quantum level. The tool used for carrying out the simulation of semiconductor nanoparticles is Band Structure lab. Band structure lab computes the electronic structure of various materials in the spatial configuration of bulk (infinitely periodic), quantum wells (confined in one dimension, infinitely periodic in 2 dimensions), and wire (confined in 2 dimensions, infinitely periodic in 3 dimensions).

Band Structure lab uses the \textit{sp}3\textit{s}*d5 tight binding method to compute \( E(k) \) for bulk, planar and nanowire semiconductors. Using this tool we can quickly compute and visualize the band structures of bulk semiconductors, thin films and nanowires for various materials, growth orientations and strain conditions. Physical parameters such as the band gap and effective mass can also be obtained from the computed \( E(k) \). The band edges and effective masses of the bulk materials and the nanostructures can be analyzed as a function of various strain conditions. Correct band structure is essential for modeling devices at nano scale.

There are various device structures available in the band structure lab. In this thesis we used nanowire device structure which is shown in fig 5.1.
After choosing the device structure we have to specify the device information such as the job type, dimensions and crystal information as shown in figures 5.1(a), 5.1(b) and 5.1(c) respectively.
All the simulations are carried on with same job type and crystal information with varying the diameter in the dimension part.
After setting the device information in the device structure next one to be considered are the TB parameters which are fixed as shown in figure 5.2. The number of bands and the number of k points are set up in the analysis part of the band structure lab as shown in figure 5.3.
Nanowire – circular cross section

Material - silicon

Diameter – 1nm

Conduction Band Minima : 2.70958 eV

Valence Band Maxima : - 1.09548 eV

Band Gap : 3.80506 eV
Diameter – 2nm

Conduction Band Minima : 1.62136 eV

Valence Band Maxima : -0.42179 eV

Band Gap : 2.04315 eV
Diameter - 3nm

Conduction Band Minima : 1.37707 eV
Valence Band Maxima : -0.237969 eV
Band Gap : 1.61504 eV
Diameter – 4 nm

Conduction Band Minima : 1.27822 eV

Valence Band Maxima : -0.145943 eV

Band Gap : 1.42416 eV
Diameter – 5 nm

Conduction Band Minima : 1.22855 eV

Valence Band Maxima : -0.102971 eV

Band Gap : 1.33152 eV
Figure 5.5: Bandgap vs. Diameter of circular nanowire of Si material.

The above graph shows the relationship between band gap energy vs. the diameter of the nanowire. The graph shows that the bandgap energy decreases as the diameter of the nanowire increases.
Nanowire circular cross section:

Material GaAs:

Diameter – 1 nm

Conduction Band Minima : 3.1153 eV

Valence Band Maxima : - 0.743422 eV

Band Gap : 3.85872 eV
Diameter – 2 nm

Conduction Band Minima : 2.2735 eV

Valence Band Maxima : -0.374384 eV

Band Gap : 2.64788 eV
Diameter – 3 nm

Conduction Band Minima : 1.93225 eV

Valence Band Maxima : -0.207769 eV

Band Gap : 2.14002 eV
Diameter – 4 nm

Conduction Band Minima : 1.77496 eV

Valence Band Maxima : -0.141927 eV

Band Gap : 1.91689 eV
Diameter – 5 nm

Conduction Band Minima : 1.68039 eV
Valence Band Maxima : - 0.101891 eV
Band Gap : 1.78228 eV
Rectangular cross section:

Material silicon:

Constant Width: 2.1 nm

Height: 2.1 nm

Conduction Band Minima: 1.52038 eV

Valence Band Maxima: -0.28251 eV

Band Gap: 1.8029 eV
Height 3.1 nm

Conduction Band Minima : 1.37852 eV
Valence Band Maxima : -0.208335 eV
Band Gap : 1.58685 eV
Conduction Band Minima : 1.31292 eV

Valence Band Maxima : -0.188971 eV

Band Gap : 1.5019 eV
Height: 5.1 nm

Conduction Band Minima: 1.28453 eV

Valence Band Maxima: -0.18111 eV

Band Gap: 1.46564 eV
Height: 6.1 nm

Conduction Band Minima: 1.26745 eV

Valence Band Maxima: -0.171291 eV

Band Gap: 1.43874 eV
Height : 7.1 nm

Conduction Band Minima : 1.25541 eV

Valence Band Maxima : -0.165269 eV

Band Gap : 1.42068 eV
Height: 8.1 nm

Conduction Band Minima: 1.2485 eV

Valence Band Maxima: -0.162069 eV

Band Gap: 1.41057 eV
Height : 9.1 nm

Conduction Band Minima : 1.24292 eV

Valence Band Maxima : -0.15868 eV

Band Gap : 1.4016 eV
Constant Height 2.1 nm

Width: 2.1 nm

Conduction Band Minima: 1.52038 eV

Valence Band Maxima: -0.28251 eV

Band Gap: 1.8029 eV
Width : 3.1 nm

Conduction Band Minima : 1.37205 eV

Valence Band Maxima : -0.209873 eV

Band Gap : 1.58193 eV
Width: 4.1 nm

Conduction Band Minima: 1.30575 eV

Valence Band Maxima: -0.170106 eV

Band Gap: 1.47586 eV
Conduction Band Minima : 1.28009 eV

Valence Band Maxima : -0.152708 eV

Band Gap : 1.4328 eV
Width: 6.1 nm

Conduction Band Minima: 1.25981 eV

Valence Band Maxima: -0.138349 eV

Band Gap: 1.39816 eV
Width: 7.1 nm

Conduction Band Minima: 1.24766 eV

Valence Band Maxima: -0.129504 eV

Band Gap: 1.37716 eV
Width: 8.1 nm

Conduction Band Minima: 1.24149 eV

Valence Band Maxima: -0.124939 eV

Band Gap: 1.36643 eV
Width : 9.1 nm

Conduction Band Minima : 1.23562 eV

Valence Band Maxima : -0.120546 eV

Band Gap : 1.35617 eV
CHAPTER 6

CONCLUSION

Pulse anodizations of aluminum were conducted under potentiostatic conditions by using $\text{H}_2\text{SO}_4$. Pulses consisting of a low-potential pulse followed by a high potential pulse were applied to achieve alternating MA and HA conditions. It was found that the effective electric field strength $E$ impressed on the barrier oxide layer has profound implications on the anodic alumina formed by high-field anodization, determining not only the chemical stability but also the mechanical properties of anodic alumina. Structural engineering of nanoporous AAO along the film growth direction can be achieved by deliberately designing pulse sequences. It is expected that the present pulse anodization process combining both MA and HA can open up a new area in nanotechnology research and may also be applied for industrial processes.
APPENDIX

FESEM IMAGES

Micro structural Images for sample 1: Top view at different magnifications
Micro Structural image for sample 1: Cross sectional view at different magnifications
Micro Structural Images for sample 2: Top view at different magnifications

Sample2_Top_01

Sample2_Top_02
Microstructural Images for sample 2: Cross sectional view at different magnifications

Sample2_Cross_BEmode_07

Sample2_Cross_BEmode_01
Micro Structural Images for sample 3: Top view at different magnifications
Micro Structural Images for sample 3: Cross sectional view at different magnifications
Micro structural Images for sample 4: Top view at different magnifications
Micro Structural Images for sample 4: Cross sectional view at different magnifications
REFERENCES


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