Development of Noble Metal Nanowires with Ultra High Surface to Volume Ratios

A thesis presented to
the faculty of
the Russ College of Engineering and Technology of Ohio University

In partial fulfillment
of the requirements for the degree
Master of Science

Isha Shrivastava
December 2013
© 2013 Isha Shrivastava. All Rights Reserved.
This thesis titled
Development of Noble Metal Nanowires with Ultra High Surface to Volume Ratios

by
ISHA SHRIVASTAVA

has been approved for
the Department of Chemical and Biomolecular Engineering
and the Russ College of Engineering and Technology by

Savas Kaya
Associate Professor of Electrical Engineering and Computer Science

Dennis Irwin
Dean, Russ College of Engineering and Technology
ABSTRACT

SHRIVASTAVA, ISHA, M.S., December 2013, Biomedical Engineering
Development of Noble Metal Nanowires with Ultra High Surface to Volume Ratios (82 pp.)
Director of Thesis: Savas Kaya

Miniaturization has become the key word for development in any research field, and “nanotechnology” is a promising technology for miniaturizing and interconnecting different areas of study whether engineering, physics, chemistry or biology. Nanostructures are filling in the empty spaces, and forming a bridge in between different areas for useful applications in biological sensors, optoelectronic devices, biomedical healthcare devices, magnetic sensors and so on. In this work, we focus on the laboratory synthesis of one such nanostructure “Nanowires”, which is produced by the bottom-up synthesis approach by the use of electrochemical deposition on aluminum substrates. The research focuses on the use of a template based technique by the formation of porous surfaces in the aluminum substrate known as anodic alumina membrane in order to facilitate the electrodeposition of noble metal nanowires. The anodization of the aluminum template by the use of different acids like oxalic acid, sulfuric acid and phosphoric acid yield different sizes of pores which provide a template for the growth of nanowires. In this research, we have used these three acids to get variety in the sizes of pores ranging from 30 nm to 200 nm. Multi-step anodization techniques yield ordered arrangement of pores providing an ordered template for electrochemical deposition of metal nanowires. Primarily noble metals like gold (Au), silver (Ag), and platinum(Pt) were used for the electrodeposition process. The morphology and structure were characterized by using microscopy techniques such as Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), and elemental analysis using Energy Dispersive Spectroscopy (EDS).
Dedicated to Mom, Dad, Bappa and Aama
ACKNOWLEDGMENTS

My two years of research journey would not have been possible without the guidance and support from my mentor and guide, my committee members, my family and my friends.

I would like to express my deepest gratitude to my advisor, Dr. Savas Kaya, for his tremendous guidance, patience, encouragement throughout my research, and providing me with an excellent atmosphere for my research. One could not wish for a better advisor than Dr. Kaya. I would like to thank Dr. Rebecca Barlag, who was more of a friend than a teacher, and who was happier than me to be in my committee. I thank my committee members Dr. Monica Burdick and Dr. Douglas Goetz for their thoughtful criticism, encouraging words, and valuable time during their busy semesters.

I would also like to thank my father Mr. Keshare Kishore Shrivastava and my mother Mrs. Lekha Shrivastava, who always believed in me and my dreams. They have had more sleepless nights than I had, thinking about my future, and their love has always been the only reason for me to move forward towards my goal with continuous dedication. I cannot forget to thank Dr. Mahendra Prasad, my uncle, who is not there in this world today, but without whom I would not be the person I am today. He is somewhere up there feeling proud for my achievements.

I would like to thank my friends back in Kathmandu and here in Athens for always being supportive and acting as stress-busters in my life. Thank you for always listening to me. My research is my baby, and I would like it to grow into something productive for the future researchers.
# Table of Contents

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
</tr>
<tr>
<td>Dedication</td>
</tr>
<tr>
<td>Acknowledgments</td>
</tr>
<tr>
<td>List of Tables</td>
</tr>
<tr>
<td>List of Figures</td>
</tr>
<tr>
<td>1 Introduction</td>
</tr>
<tr>
<td>1.1 Nanostructures</td>
</tr>
<tr>
<td>1.2 Nanowires</td>
</tr>
<tr>
<td>1.2.1 Types of Nanowires</td>
</tr>
<tr>
<td>1.3 Fabrication Methods</td>
</tr>
<tr>
<td>1.4 Metallic Nanowires</td>
</tr>
<tr>
<td>1.5 Template Based Synthesis of Metallic Nanowires</td>
</tr>
<tr>
<td>1.6 Electrochemical Deposition</td>
</tr>
<tr>
<td>2 Background</td>
</tr>
<tr>
<td>2.1 Nanoporous Alumina Membranes</td>
</tr>
<tr>
<td>2.1.1 Aluminum(III)Oxide [ Al₂O₃]</td>
</tr>
<tr>
<td>2.1.1.1 Introduction</td>
</tr>
<tr>
<td>2.1.2 Formation of Oxide Layers on Aluminum</td>
</tr>
<tr>
<td>2.2 Anodic Aluminum Membrane (AAO)</td>
</tr>
<tr>
<td>2.3 Voltage–Current (V-I) Dependence of AAO</td>
</tr>
<tr>
<td>2.4 Electrochemical Synthesis of Alumina Membranes : Electropolishing of Aluminum</td>
</tr>
<tr>
<td>2.5 Formation Mechanism of Nanoporous Alumina</td>
</tr>
<tr>
<td>2.5.1 Barrier Layer formation</td>
</tr>
<tr>
<td>2.5.2 Stages of Nanoporous Alumina Formation</td>
</tr>
<tr>
<td>2.6 Models for Explaining Pore Nucleation Mechanism</td>
</tr>
<tr>
<td>2.7 Hexagonal Self Ordering</td>
</tr>
<tr>
<td>2.8 Factors Controlling the Self Ordering of Hexagonal Pores</td>
</tr>
<tr>
<td>2.8.1 Effect of Acid Type and Concentration</td>
</tr>
<tr>
<td>2.8.2 Effect of Anodizing Voltage</td>
</tr>
<tr>
<td>2.8.3 Effect of Temperature</td>
</tr>
</tbody>
</table>
3 Experimental Techniques ................................................. 39
  3.1 First Step Anodization ............................................. 39
  3.2 Chemical Etching of Alumina ..................................... 41
  3.3 Multi-step Anodization ............................................ 42
  3.4 Post Treatment of Anodic Alumina ............................... 43
      3.4.1 Pore Widening ............................................ 43
  3.5 Electrodeposition ................................................... 44
  3.6 Characterization of the Performance and Properties of Nanostructures .... 48
      3.6.1 Atomic Force Microscope .................................. 50
      3.6.2 Scanning Electron Microscope ............................. 53
      3.6.3 Energy Dispersive Spectroscopy ........................... 55

4 Observations and Analysis ............................................. 56
  4.1 Oxalic Acid ......................................................... 56
  4.2 Sulfuric Acid ....................................................... 65
  4.3 Phosphoric Acid .................................................... 67

5 Concluding Remarks and Future Considerations ........................ 72
  5.1 Conclusion ......................................................... 72
  5.2 Future consideration ............................................... 72

References ................................................................. 74
## List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Physio-chemical changes in properties between gold and gold nanoparticles.</td>
</tr>
<tr>
<td>2.1</td>
<td>Major acid types and their concentration used for formation of different pore sizes.</td>
</tr>
<tr>
<td>3.1</td>
<td>Different types of acids used during the first step anodization process.</td>
</tr>
<tr>
<td>3.2</td>
<td>Different types and concentration of acid used during the second step anodization process.</td>
</tr>
<tr>
<td>3.3</td>
<td>Electrodeposition solutions used for the deposition of Au, Ag, and Pt and the different voltage conditions.</td>
</tr>
<tr>
<td>4.1</td>
<td>Anodization and intermediate conditions before electrodeposition on aluminum samples for oxalic acid.</td>
</tr>
<tr>
<td>4.2</td>
<td>Anodization and intermediate conditions before electrodeposition on aluminum samples for sulfuric acid.</td>
</tr>
<tr>
<td>4.3</td>
<td>Comparison of pore sizes for different acids before and after pore widening.</td>
</tr>
<tr>
<td>4.4</td>
<td>Anodization and intermediate conditions before electrodeposition on aluminum samples for phosphoric acid.</td>
</tr>
</tbody>
</table>
# List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Moore’s law [9].</td>
</tr>
<tr>
<td>1.2</td>
<td>Comparison of size dependence of surface to volume ratios. Nanoparticles have more surface area to volume ratio than their bulk counterparts [13].</td>
</tr>
<tr>
<td>1.3</td>
<td>Characterization of nanomaterials based on their dimensionality [16].</td>
</tr>
<tr>
<td>1.4</td>
<td>Different fabrication approaches and methods in nanofabrication [32].</td>
</tr>
<tr>
<td>1.5</td>
<td>Schematic representation of a electrochemical cell for electrodeposition [41].</td>
</tr>
<tr>
<td>1.6</td>
<td>Schematic diagram showing cylindrical pores used for restrictive template based methods for deposition of nanowires [42].</td>
</tr>
<tr>
<td>1.7</td>
<td>Synthesis of nanoparticle arrays by active template assisted electrodeposition [41].</td>
</tr>
<tr>
<td>2.1</td>
<td>Voltage dependence of the pores formed in AAO [43].</td>
</tr>
<tr>
<td>2.2</td>
<td>Optical Microscopic Images depicting the surface smoothness with (a,b,c,d) and without electropolishing (e) [48].</td>
</tr>
<tr>
<td>2.3</td>
<td>Electropolishing set-up (left) and electropolished Aluminum (right).</td>
</tr>
<tr>
<td>2.4</td>
<td>Formation mechanism of the barrier layer [43].</td>
</tr>
<tr>
<td>2.5</td>
<td>Stages explaining the formation of the nanoporous alumina membrane [46].</td>
</tr>
<tr>
<td>2.6</td>
<td>Pore formation mechanism in aluminum substrate [43].</td>
</tr>
<tr>
<td>2.7</td>
<td>Schematic showing the hexagonal pore ordering, where Dp = pore size and Dc = cell size [50].</td>
</tr>
<tr>
<td>2.8</td>
<td>Cell diameter versus anodizing voltage for different acids used during anodization [46].</td>
</tr>
<tr>
<td>3.1</td>
<td>Typical anodization setup for porous alumina formation.</td>
</tr>
<tr>
<td>3.2</td>
<td>Setup used in the laboratory for anodization of aluminum.</td>
</tr>
<tr>
<td>3.3</td>
<td>A diagrammatic representation of the alumina pores before (a) and after (b) the pore widening process [52].</td>
</tr>
<tr>
<td>3.4</td>
<td>Electrodeposition setup including the electrodeposition chamber, magnetic stirrer/heater and the potentiostat/galvanostat.</td>
</tr>
<tr>
<td>3.5</td>
<td>Electrochemical cell for electrodeposition process.</td>
</tr>
<tr>
<td>3.6</td>
<td>Schematic showing the electrodeposition process [54].</td>
</tr>
<tr>
<td>3.7</td>
<td>Two step anodization procedure of Aluminum [43].</td>
</tr>
<tr>
<td>3.8</td>
<td>Schematic of atomic force microscope [57].</td>
</tr>
<tr>
<td>3.9</td>
<td>Plot of force as a function of probe-sample interaction in the different modes of AFM [57].</td>
</tr>
<tr>
<td>3.10</td>
<td>Complete setup of the AFM Agilent 5500 LS.</td>
</tr>
<tr>
<td>3.11</td>
<td>Schematic of the scanning electron microscope [58].</td>
</tr>
<tr>
<td>3.12</td>
<td>Complete setup of the SEM from the manufacturer JEOL - JSM.6400.</td>
</tr>
</tbody>
</table>
4.1 Two step anodization with well-ordered arrangement of pores with the anodization conditions of 15 mins of first step anodization, 30 mins of chemical etching, 30 mins of second step anodization and 34 °C and 90 mins of pore widening observed under a) AFM and b) SEM. .......................... 56

4.2 Electrodeposition of Au nanowires on oxalic acid template under potentiostatic conditions with a voltage of -0.9 V for 12 mins. .......................... 57

4.3 Au nanowires on three step anodized template with 15 mins first step anodization, 30 mins chemical etching, 15 mins second step anodization, 30 mins chemical etching and 30 mins of third step anodization. .................. 58

4.4 Converging nanowires due to prolonged electrodeposition times. .................. 58

4.5 Silver nanowires deposition on the AAO template anodized with oxalic acid with 15 mins of first step anodization, 30 mins of chemical etching and 30 mins of second step anodization. .......................... 60

4.6 Platinum electrodeposition after pore widening of 35 °C for 90 mins and -0.55 V for 11 minutes from a mixture of H₂PtCl₆ and HCl in the ratio of 1:1. .... 61

4.7 a) Random distribution of platinum chunks along the surface of the pores. b) Decrease in platinum chunks alongside the surface of AAO moving from circumference to the centre .......................... 61

4.8 Platinum chunks magnified to show the texture. The electrodeposition was carried out by using 100 V peak-peak voltage, 100 Hz AC signal and -0.55 V DC offset voltage for 9 minutes. .......................... 62

4.9 Uneven distribution of platinum chunks on the surface on AAO membrane with DC electrodeposition conditions of -0.75V for 15 mins. .................. 63

4.10 EDS analysis showing the platinum peaks. .......................... 64

4.11 Two step anodization of aluminum sample with 0.3 M sulfuric acid under anodization conditions of 15 mins first step anodization, 30 mins chemical etching, 30 mins second step anodization and 34 °C and 90 mins of pore widening as observed under the AFM. .......................... 66

4.12 Distribution of Au nanowires in AAO membrane with 0.3 M sulfuric acid solution with electrodeposition timings of -0.9 V for 17 mins. .................. 67

4.13 Attempts to deposit Ag nanowires on AAO template performed by using 0.3 M sulfuric acid. .......................... 68

4.14 Pores on aluminum substrate grown with 0.1 M phosphoric acid under 15 mins of first step anodization, 30 mins chemical etching, 30 mins of second step anodization as observed under AFM. .......................... 69

4.15 Pores on aluminum substrate grown with 0.1 M phosphoric acid under 15 mins of first step anodization, 30 mins chemical etching, 30 mins of second step anodization and b) 60°C and 30 mins of pore widening. .................. 70

4.16 Pores on aluminum substrate grown with 0.1 M phosphoric acid under 15 mins of first step anodization, 30 mins chemical etching, 30 mins of second step anodization and 34 °C 60 mins of pore widening and b) Top view of the overall pore structure of phosphoric acid sample with two step anodization. .......................... 71
1 INTRODUCTION

A small word with a big potential has been quickly spreading itself into different areas of human life - that word is "nano". Although the nano-world is built on the dimensions as small as billionth of a meter, it is an area of scientific development that promises "more for less"[1]. Nanotechnology refers to the science of creating, designing, producing, and using structures and devices that have dimensions in the nanometer scale [2]. Also referred to as "Atomically Precise Technology" (APT), it visualizes atoms as the building block to control the architecture, composition, physical, and chemical properties of their bulk counterparts [3]. The US Foresight Institute refers, "Nanotechnology is a group of emerging technologies in which structure of matter is controlled at the nanometer scale to produce novel materials and devices that have useful and unique properties"[3].

The credit for introducing the term nanotechnology goes to Nobel Laureate Richard Feynman who mentions in his epic lecture in the year 1959 the possibility of maneuvering things on an atomic scale [4]. This vision of Feynman had led to some of the important discoveries, and a development that couldn’t be avoided [5]. If Feynman is considered to be the philosopher, then Eric Drexler who expanded Feynman’s definition in his book, “Engines of Creation, the Coming Age of Nanotechnology”[6] is considered to be the Prophet.

The central idea of nanotechnology is "Smaller is Better", and miniaturization has been the heart of innovation. Moore’s Law of miniaturization would serve as the best example for the initiation in the advancement of making devices smaller [7]. Gordon E. Moore had predicted in his paper in 1965, that the number of transistors that would fit on a given area of silicon would double every two years as illustrated in Figure 1.1 [8, 9]. However, since the scaling down of the technology is expected to slow down in the coming years, the concept of building up through self assembly of atomic and molecular building blocks has emerged as an alternative for manufacturing devices.
1.1 Nanostructures

Nanostructures are defined as objects having at least one critical dimension less than 100 nm and exhibiting new physicochemical properties, which are different from the same material in bulk. From applications ranging from medical to clean energy solutions, nanostructures have taken the world of science and technology by storm [10].

Mihail Roco of the U.S. National Nanotechnology Initiative has divided the promising area of nanotechnology and its applications into four generations. The first generation of nanostructures include passive nanostructures with materials designed to perform a single task, for e.g. dispersed and contact nanostructures like aerosols, colloids. The second generation of nanostructures includes active nanostructures with bio-devices and actuators. The third generation includes the system of nanosystems with 3 D
networking and new hierarchical architectures. The fourth generation comprises of molecular nanosystems. Today, the level of advancements in the world of nanotechnology has led to developing the third generation of nanostructures [11].

The most significant question here is the importance of nanostructured materials in comparison to their bulk counterparts. Nanostructures can be considered as a bridge between molecules and bulk materials. Therefore, when the size approaches the atomic scale, the physical laws associated with the materials change from classical to quantum-mechanical based laws [12]. The appearance of the quantization effects is primarily due to the confinement of the movement of electrons.

The change in properties of the nanomaterials can be attributed to the relatively large surface area as compared to the bulk form as shown in Figure 1.2 [13]. The decrease in size of the particles introduces a greater fraction of atoms on the surface as compared to inside. Since the surface area per unit mass increases, it exposes a greater amount of the material for reacting with available atoms or ions thus translating to a very high surface reactivity, which is ideal for catalysis or sensor applications.

In addition to the surface area effects, quantum effects dominate the properties of nanomaterials with the reduction in size. Changes in thermal properties such as melting temperature, mechanical properties such as adhesive and capillary forces, optical properties such as absorption and scattering of light, and electrical and magnetic properties such as tunneling current and superparamagnetic effects become predominant at the nanoscale [14]. Some changes in properties at nanoscale for gold are demonstrated in Table 1.1 [15]. Biological systems correspond to the systematic arrangement of nanoscale materials, for example the size of proteins is 1-20 nm, and the diameter of DNA is 2.5 nm, which gives us the ability to fabricate materials in this regime, and holds promise for artificial components within cells.
Figure 1.2: Comparison of size dependence of surface to volume ratios. Nanoparticles have more surface area to volume ratio than their bulk counterparts [13].

Table 1.1: Physio-chemical changes in properties between gold and gold nanoparticles.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Gold (Au)</th>
<th>Au nanoparticle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>Yellow</td>
<td>Red</td>
</tr>
<tr>
<td>Electrical Conductivity</td>
<td>Conductive</td>
<td>Loses conductivity at 1–3 nm</td>
</tr>
<tr>
<td>Magnetism</td>
<td>Non-magnetic</td>
<td>Becomes magnetic at 3 nm</td>
</tr>
<tr>
<td>Chemical Reactivity</td>
<td>Chemically inert</td>
<td>Explosive and catalytic</td>
</tr>
</tbody>
</table>

Nanoparticles fall into three major categories in terms of their origin. They are naturally occurring, incidental and engineered. Some of the naturally occurring
Nanoparticles include sea spray, mineral composites, volcanic ash and viruses; incidental nanoparticles, which are formed as a result of man-made industrial processes include welding fumes, industrial effluents; engineered nanoparticles are the result of scientific development such as quantum dots, buckyballs, nano-capsules and so on [15].

Nanoparticles can be classified based on their dimensionality, morphology, composition and uniformity. Based on their dimensionality, they can be characterized as zero dimensional, one dimensional, two dimensional and three dimensional. Zero dimensional nanomaterials are the simplest building block in nanomaterials design in which the nanoparticles are isolated from each other [16]. Some examples of zero dimensional nanomaterials are nanocluster materials and nanodispersions.

One dimensional (1D) nanomaterials consist of nanotubes, nanowires and nanorods with length ranging from 100 nm to tens of microns. One dimensional nanomaterials are an increasing interest in the scientific society owing to the fact that they have a wide range of potential applications. For example, two dimensional (2D) nanomaterials include nanoprisms, nanoplates, nanosheets, nanowalls, nonocoatings, and have two dimensions outside the nanomateric size range. These nanomaterials show unique shape dependent characteristics, and are an important part in building sensors, photocatalysts, nanocontainers and nanoreactors [17].

Three dimensional (3D) nanomaterials on the other hand, are used in the area of catalysis, magnetic material and electrode material for batteries. In such nanostructures the 0D, 1D and 2D structural elements form interfaces due to close proximity with each other. Examples of three dimensional nanomaterials are multi-layered and poly-crystalline materials [16]. An illustrative diagram along with microscopic images of the 0D, 1D, 2D and 3D nanomaterials are shown [14, 15] in Figure 1.3 [16].

The properties of nanoparticles such as large surface-to-volume ratios and their ability to bind to other molecules provides them with a unique ability to diagnose and treat
Figure 1.3: Characterization of nanomaterials based on their dimensionality [16].

A variety of diseases with higher efficacy and fewer side effects than the existing methods. Due to their extremely small size, which is comparable to individual cells and viruses, nanomaterials are suitable for therapeutic delivery at molecular level along with application of external fields such as near infrared light or radiofrequency waves [18].

Surface modification or functionalized nanoparticles have shown great potential in their usage in biological and biomedical applications for bio-imaging, bio-sensing, single-molecule tracking, drug delivery, and transfection [19]. Soklov et al. have investigated the use of gold nanoparticles in conjunction with an antibody to bind to epidermal growth factor receptors which are over-expressed in cervical cancer cells. Since, gold nanoparticles possess surface plasmon resonance scattering behavior they can be useful for the detection of such cervical cancer cells [19]. Cerium oxide nanoparticles act as an antioxidant removing the oxygen free radicals present in patients blood after a traumatic injury [20]. Nanoparticles have been used to deliver vaccine, which protects the vaccine allowing it to be in the body for a longer period of time to trigger a stronger immune response. Carbon nanoparticles, also referred to as nanodiamonds have a great potential in their use with protein molecules to enhance bone growth around dental or
joint implants. Nickel nanoparticles in conjunction with polymer have been identified as a suitable synthetic skin with self-healing and pressure sensing capabilities. The change in electrical resistance along with pressure changes gives it the sensing abilities.

Numerous properties of one-dimensional nanomaterials, nanowires, nanotubes and nanorods have been identified which makes them an ideal structure for electron transport and nanoscale sensing [21]. The motivation for looking into the application of nanowires in the biomedical field is the compatibility of its dimensions with the mammalian cells [22]. Nanowires have been shown to be used for high-quality and fast diagnosis of diseases with the development of biosensors, and drug delivery with targeted delivery of therapeutic reagents. The optical properties of gold nanorods can be used to develop lab-in-a-tube biosensors for detection of biological targets. Individual Zinc oxide nanowires have been used as an electrochemical biosensor for uric acid [23]. Proteins and nucleic acids which are usually charged in an aqueous solution can be detected by means of nanowire sensors when appropriate receptors are linked to the nanowire surface [24]. Due to the charge conduction ability of nanowires, it is easy to identify virus bound to an antibody receptor on a nanowire device due to the fact that the conductance of the device changes from its baseline value after the attachment of the virus, and returns to the baseline value when the virus unbinds itself.

1.2 Nanowires

Nanowires are 1D nanostuctures through which electrons and excitons can be efficiently transported, and therefore are considered to be an important element in the assembly of nanoelectronic and nanooptoelectronic devices [25]. The lateral size of nanowires may be constrained to tens of nanometers or less; however, they have unconstrained longitudinal size. Nanowires, also referred to as “quantum wires” [26], can be either suspended, deposited or synthesized from the elements [27].
A suspended nanowire is chemically etched in an evacuated chamber by using high speed atoms or ions in order to reduce its diameter. The use of high temperature near the melting point of the wire, and stretching it is another way of producing such nanowires [28]. Deposited nanowires can be fabricated on non-metallic surfaces like plastic or glass in the same manner as semiconductor chips are grown.

Ordered nanowires can be classified into several structural classes of helical nanowires, molecular nanowires, and nanocrystalline nanowires. Generally, helical nanowires may be filled nanotubes; molecular nanowires may be fragments of quasi-1D crystals and nanocrystalline nanowires are 1D fragments of bulk crystals [29]. These nanocrystalline nanowires can be further characterized as twinned, core shell and longitudinally heterogeneous nanowires.

1.2.1 Types of Nanowires

There are different types of nanowires, which can be classified as metallic nanowires e.g. gold (Au), nickel (Ni), platinum (Pt) and so on, semiconducting nanowires e.g. silicon (Si), indium phosphide (InP), gallium nitride (GaN) and so on, insulating nanowires e.g. silicon dioxide (SiO₂), titanium dioxide (TiO₂), and molecular nanowires consisting of molecular units, which maybe either organic e.g. deoxyribonucleic acid (DNA) or inorganic [30].

1.3 Fabrication Methods

Fabrication of nanomaterials can be broadly classified into two methods: top-down fabrication method and bottom-up fabrication method. Top-down fabrication method is a subtractive process in which the nanomaterials are derived by continuous removal of the bulk material until the desired nanosized material is obtained [31]. A simple way to understand this would be imagining a statue carved out of a huge square block of marble.
Some of the examples of top-down fabrication methods are ball milling, dry etching, lithography and so on.

Bottom-up fabrication method is an additive process that includes assembling the atoms and molecules or the smallest precursors of the nanomaterial until the desired nanosized material is formed [31]. Some of the examples of bottom-up methods are chemical vapor deposition, molecular beam epitaxy, spray pyrolysis and so on. The overall fabrication methods of nanowires are shown in the hierarchical chart in Figure 1.4 [32].

![Fabrication techniques of Nanomaterials]

Figure 1.4: Different fabrication approaches and methods in nanofabrication [32].

There are different techniques that are designed to synthesize and fabricate 0D, 1D, 2D and 3D nanostructured materials with controlled shape, size, dimensionality and structure [17]. The bottom-up fabrication techniques can be further classified into gaseous phase methods, liquid phase methods, solid phase methods, and biological methods.
1.4 Metallic Nanowires

Metallic nanowires are mainly important due to their wide use as nanoscale interconnects, and as one of the active components of electronic and electromechanical devices [33]. Metal nanowires have diameters ranging from a single atom to a few hundred nanometers; and, the lengths vary over a range of a few atoms to microns [34]. The length to diameter (width) ratio, also known as the aspect ratio, describes some of the characteristic properties of metallic nanowires. Nanowires usually refer to wires with larger aspect ratio, greater than 20, while wires having smaller aspect ratios are called nanorods. Nanocontacts, another form of nanowires are short wires that are bridged in between two large electrodes.

There are different techniques that are developed for the synthesis of 0D, 1D, 2D and 3D nanostructures; however, techniques for fabrication of metallic nanowires can be generally grouped into four categories. They are spontaneous growth techniques, template-based synthesis, electro-spinning and lithography [14].

Spontaneous growth techniques include evaporation condensation, dissolution condensation, vapor-liquid-solid growth (VLS), and stress-induced re-crystallization. Template based synthesis, which will be discussed in detail includes electroplating and electrophoretic deposition, colloid dispersion, melt, or solution filling, and conversion with chemical reaction [14].

1.5 Template Based Synthesis of Metallic Nanowires

Most of the methods of nanowire production result in random orientation of nanowires; however, in template based growth, the density, diameter and length of the nanowires can be controlled independently [35]. Template-based synthesis of nanowires is a solution or a colloidal dispersion process, which is least expensive, and more feasible for mass production. A suitable template must have a surface, edge, channel or volume
serving as a platform for the synthesis of nanowire; it should be able to detach from the produced nanomaterials by either physical or chemical means, and should be inexpensive and recyclable [36].

Various attributes need to be considered when choosing a suitable template for nanowire production. The life of a template must be greater than the reaction time being applied; the template must be stable with respect to reaction conditions, and it should act as a suitable medium for positioning nanomaterials in an ordered manner.

There are different types of templates that are being used for the synthesis of nanowires: the soft template (pseudo-template) and the hard template. The soft template consists of organic surfactants, polymers, and biological viruses that have flexible shape. These templates provide cavities into which the substances can diffuse through the cavity wall [37, 38]. Hard templates have well defined channels in the form of pores, channels or hollow spaces, and the substances can enter the channel from its opening. Examples of hard templates are mesoporous nanomaterials, porous alumina, proteins, porous silicon templates and so on. Usually “template synthesis” refers to hard template synthesis using an anodic alumina membrane (AAO), which is the primary synthetic method discussed in the thesis.

There are primarily five different strategies for carrying out the template assisted synthesis of nanowires namely electrochemical deposition, electroless deposition, chemical polymerization, sol-gel deposition and chemical vapor deposition [39].

1.6 Electrochemical Deposition

Template electrodeposition synthesis offers numerous advantages over other synthesis methods for the production of one-dimensional nanostructures. It does not require high temperature, vacuum or expensive instruments and can be performed under normal conditions. Templated electrodeposition not only has a higher growth rate but also
has the ability to control the morphology of deposited materials by controlling the shape of the template pores. It is easier to form multi-segmented materials by depositing two or more components into the membrane [40].

Electrochemical deposition involves the reduction of charged growth species from the electrolyte at the deposition surface that serves as one of the electrodes. Application of an external electric field between two different electrodes induces electrochemical reactions to occur at both electrodes. Hence, the electrical energy is converted into chemical potential, which is also known as electrolysis. The oxidation reaction takes place at the anode, which is connected to the positive side, and the reduction reaction takes place at the cathode, which is connected to the negative side of the connected power supply. The electrolytic deposition occurs at cathode, and in general terms is referred to as electrochemical deposition or electrodeposition [35]. This technique is only applicable to certain materials like metals, alloys, semiconductors and electrical conductive polymers.

Electrodeposition technique is usually carried out in an electrochemical cell that requires application of a controlled current at a certain required voltage. The cell has a reference electrode, a cathode and an anode (counter electrode) as shown in Figure 1.5[41]. The growth of nanowires occurring at the cathode is a self-propagating process. The current, however, doesn’t change much during the entire process except when the pores become completely filled because of increased contact with the electrolyte solution.

A wider approach for classification template based electrodeposition methods comprises of negative template methods, positive template methods, and surface step templates [34]. The negative template methods, also known as restrictive template based electrodeposition, consist of cylindrical nanopores as shown in Figure 1.6 [42] or channels of an inert, non-conductive nanoporous electrode material in a solid material. The diameter of the nanopores determines the type and nature of the nanowires. Free-standing
Figure 1.5: Schematic representation of an electrochemical cell for electrodeposition [41].

Nanowires can be obtained by dissolving the template. Examples of negative templates are track etched membranes, anodic porous alumina and so on.

Figure 1.6: Schematic diagram showing cylindrical pores used for restrictive template based methods for deposition of nanowires [42].
Positive template methods use DNA and carbon nanotubes as templates, which are usually wire type, and the outer surface of the template serves as the platform for the formation of nanowires. Unlike negative template methods, the diameter of the nanowires is not controlled by the template sizes. Surface step-edge template based electrodeposition, or active template-assisted electrodeposition, starts at the step edges as shown in Figure 1.7 or at defect sites [41].

Figure 1.7: Synthesis of nanoparticle arrays by active template assisted electrodeposition [41].

In our research, we focus mainly on the use of anodic porous alumina as the negative template method for the electrodeposition of various metallic nanowires.
2 BACKGROUND

2.1 Nanoporous Alumina Membranes

2.1.1 Aluminum(III)Oxide [ Al₂O₃ ]

2.1.1.1 Introduction

Aluminum, which is the third most abundant element in the earth’s crust, constitutes of about 8% [43] by weight of the earth’s surface. Aluminum is a unique metal due to its light weight, and anticorrosion properties [44]. However, since it reacts very easily with the oxygen in the atmosphere, it is usually found in combination with other materials. Extracted from its primary ore bauxite, the important compounds of aluminum are considered to be its oxides and sulfates. Alumina (Al₂O₃), is the most commonly known stable oxide of aluminum which contains 52.8 % of aluminum by weight.

2.1.2 Formation of Oxide Layers on Aluminum

Aluminum is a reactive metal that reacts with oxygen and water vapor when exposed to them to create a thin nanometer-sized oxide layer. This oxide layer formed on top of aluminum maybe both amorphous or crystalline at temperatures above 500 °C, preventing further dissolution of aluminum by acting as a protective barrier layer. The reactions that occur during the process are represented in Equations 2.1 and 2.2:

\[ 4Al + 3O_2 = 2Al_2O_3 \]  \hspace{1cm} (2.1)

\[ 2Al + 3H_2O = Al_2O_3 + 3H_2 \]  \hspace{1cm} (2.2)

The corrosive oxide layer formed on ferrous metal surfaces is different than the protective oxide layer formed on aluminum, enabling it to be used for a variety of industrial applications.
It is seen that the anodic film reacts further with the environment forming a hydrated porous layer on top of the inert dense layer. Hence, the oxide structure comprises of two distinct layers, one being the porous hydrated AAO layer, and the other inert dense layer known as the barrier layer [43].

2.2 Anodic Aluminum Membrane (AAO)

The hexagonal pores in AAO were first reported around 1950’s. After four years, the porous oxide layer was fabricated in labs, and its structure was verified [45]. The regular self-organized porous oxide layer is formed by the anodization of aluminum in acidic media with certain concentration and fixed voltages. There are different factors that determine the pore size and structure that will be discussed later. The porous nanostructures are insulators, optically transparent, chemically stable and bio compatible materials. Due to their insulating nature, these porous membranes are used as a convenient template for the fabrication of free-standing metallic nanowires.

Some of the important features of AAO include a highly ordered array of pores, the flexibility in changing the pore diameter from a few nanometers to a few hundred nanometers, and a high pore density of around $10^{10} - 10^{12}$ pores/cm$^2$ [46]. Porous alumina membranes also possess mechanical, thermal, and optical properties, and can be treated with both organic and inorganic solutions, which is another reason AAO is an ideal material used as a template [47].

2.3 Voltage–Current (V-I) Dependence of AAO

As represented in Figure 2.1, the effects of voltage and current on the aluminum sample depicts the necessity for suitable V–I conditions in order for the formation of AAO [43]. At high currents and low voltages, pitting begins at the crystallographic boundaries; increasing the voltage and reducing the current results in electropolishing of the aluminum sample. Further increase of voltage then results in decrease in current and formation of a
porous oxide layer. Finally, at maximum voltage and lowest level of current, a thick layer of aluminum oxide is formed [45].

![Figure 2.1: Voltage dependence of the pores formed in AAO [43].](image)

2.4 Electrochemical Synthesis of Alumina Membranes: Electropolishing of Aluminum

Formation of an ordered array of nanopores on an alumina membrane requires several process and pre-treatments. The nanopores formed on the substrate depend on the initial quality of the aluminum substrate, the surface structure, and surface roughness. Initially, the aluminum substrate will have a pre-existing layer of oxide on its surface due to the presence of oxygen and water vapor in the atmosphere. Industrially obtained aluminum foils will have surface defects, scratches, and impurities. The surface treatment of aluminum is one of the essential steps for formation of an ordered arrangement of pores due to the fact that the pore nucleation mechanism comprises of both random nucleation and nucleation from surface defects and grain boundaries. The presence of other elements in aluminum not only reduces the formation of the oxide layer during the anodization
process but also affects the structure of the oxide layer during the process. As shown in Figure 2.2 a-d, electropolishing changes the surface properties making it smoother and more uniform. Figure 2.2 e, represents an unelectropolished sample that cannot be used for anodization steps due to the fact that the surface defects would not allow uniform growth of pores[48].

In the laboratory, polycrystalline aluminum foils with 0.13 mm(0.005 inches) thickness and 99.9995% purity are used. The electropolishing solution is prepared by using perchloric acid and ethanol in the ratio of 1:5. The concentrations of perchloric acid and ethanol used in the laboratory are 70% by volume and 95% by volume respectively. For the anode and cathode arrangement, platinum mesh was used as the cathode and 1.5
cm × 1.5 cm cut aluminum foils were used as the anode. The electropolishing setup and the electropolished aluminum are shown in Figure 2.3.

Figure 2.3: Electropolishing set-up (left) and electropolished Aluminum (right).

### 2.5 Formation Mechanism of Nanoporous Alumina

#### 2.5.1 Barrier Layer formation

Barrier layer is a non-porous layer that is usually insoluble or dissolves at a slower rate than it is formed. Formation of a complete barrier layer requires a pH of 7 or more, and an acidic pH is generally required for the formation of porous alumina layer. Barrier layer formation generally consists of two stages: supply of constant current results in linear increase of voltage, and this increase continues until it reaches a constant formation voltage; in the second stage, in order to maintain the voltage, the Al" ions migrate from the metal surface to the electrolyte and the O" and OH" ions migrate inward. This mechanism is shown in Figure 2.4[43]. This oxide growth occurs at the metal-oxide
interface and oxide-electrolyte interface with 60% of the growth occurring at the metal-oxide interface. When the rate of oxide growth increases, the resistance continues to increase which in turn decreases the flow of current. The oxide layer formation then ceases and the width remains constant. This oxide layer prevents any further contamination or reaction with the environment forming a hard, wear-resistant, insulating layer commonly known as the barrier layer [43].

Figure 2.4: Formation mechanism of the barrier layer [43].

2.5.2 Stages of Nanoporous Alumina Formation

The mechanism of nanoporous alumina formation is mainly explained in Refs. [43, 46, 49]

Stage I: Initial application of voltage causes the aluminum oxide layer to form by the oxidation of metal aluminum by the oxide containing ions from the electrolyte. In the presence of the natural oxide layer, the ionic mobility is high between the oxide-electrolyte interface due to high current flow. During this stage, around 70% of the Al\(^{3+}\) ions and O\(^{2-}\) ions contribute to the formation of the barrier layer. Due to increase in the metal-oxide
interface, the thickness of the barrier layer increases and hence prevents the ion transfer and oxidation. The anodization current at this stage decreases as shown in Figure 2.5 [46].

**Stage II**: Before the formation of pores, pits and cracks appear at the oxide-electrolyte interface. Pores generally nucleate at the defect areas, grain boundaries or depressions on the surface. Due to the local dissolution of the oxide by the hydrogen containing ions in the electrolyte, fine featured pores begin to develop. The application of voltage results in formation of individual paths to form nanopores with a high pore density. During the formation of this layer, the barrier layer regenerates with further oxide growth to form a semi spherical shaped oxide layer of constant thickness, also known as the pore bottom. Rate of oxidation is greater than the oxide dissolution rate at this stage.

**Stage III**: Formation of pores is gradually stabilized in the passage of time. Pores either increase in size, by merging with adjacent pores or become effective dissolution sites.

**Stage IV**: At this stage, the rate of dissolution equals, the rate of oxidation and the corresponding anodization current reaches a fixed value. The metal–oxide and oxide-electrolyte interface attain a constant speed with the stabilization of pore structure.

The formation of the porous oxide layer and the aluminum dissolution can be represented by the following equations 2.3 to 2.7. The formation of the porous oxide layer is initiated by the dissolution of aluminum and the reaction is presented by

\[
2Al \rightarrow 2Al^{3+} + 6e^- \tag{2.3}
\]

The electrons from the dissolution due to reaction at cathode produce hydrogen gas

\[
6H^+ + 6e^- \rightarrow 3H_2(g) \tag{2.4}
\]

The anodic reaction between the metal-oxide interface is represented by

\[
2Al + 3O^{2-} \rightarrow Al_2O_3 + 6e^- \tag{2.5}
\]
Another oxide-electrolyte boundary where Al cations react with water molecules is presented by

$$2Al^{3+} + 3H_2O \rightarrow Al_2O_3 + 6H^+ \quad (2.6)$$

The summary of overall anodization of aluminum is represented by

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2 \quad (2.7)$$
The formation of nanoporous alumina results from anodization for which a wide range of acids have been used and experimented by many researchers. The type of application determines the use of different types and combination of acids. Table 2.1 presents the types of acids used for nanoporous alumina growth in the aluminum substrate[43]:

Table 2.1: Major acid types and their concentration used for formation of different pore sizes.

<table>
<thead>
<tr>
<th>Main Acid Used in Electrolysis</th>
<th>Molecular Formula</th>
<th>Concentration (M)</th>
<th>Pore Size Range (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic</td>
<td>CH₃CO₂H</td>
<td>1</td>
<td>Not specified</td>
</tr>
<tr>
<td>Citric</td>
<td>HO₂CCH₂(OH)(CO₂H)CH₂CO₂H</td>
<td>0.1–2</td>
<td>90–250</td>
</tr>
<tr>
<td>Chromic</td>
<td>H₂CrO₄</td>
<td>0.3–0.44</td>
<td>17–100</td>
</tr>
<tr>
<td>Glycolic</td>
<td>CH₃(OH)CO₂H</td>
<td>1.3</td>
<td>35</td>
</tr>
<tr>
<td>Malic</td>
<td>HO₂CH₂CH(OH)CO₂H</td>
<td>0.15–0.3</td>
<td>Not specified</td>
</tr>
<tr>
<td>Malonic</td>
<td>CH₂(CO₂H)₂</td>
<td>0.1–5</td>
<td>Not specified</td>
</tr>
<tr>
<td>Oxalic</td>
<td>C₂H₂O₄</td>
<td>0.2–0.5</td>
<td>20–80</td>
</tr>
<tr>
<td>Phosphoric</td>
<td>H₃PO₄</td>
<td>0.04–1.1</td>
<td>30–235</td>
</tr>
<tr>
<td>Sulfuric</td>
<td>H₂SO₄</td>
<td>0.18–2.5</td>
<td>12–100</td>
</tr>
<tr>
<td>Tartaric</td>
<td>HO₂CCH(OH)CH(OH)CO₂H</td>
<td>0.1–3</td>
<td>Not specified</td>
</tr>
</tbody>
</table>

The electrolyte used in the process of anodization has a very significant part to play in the formation of porosity and permeability of the membrane. The electrolyte should be able to maintain a flow of Al³⁺ ions from the metal substrate into the electrolyte. This flow of Al³⁺ ions is maintained mainly by the applied electric field, which causes the direct expulsion of ions, and the direct dissolution of the forming oxide layer [43].
2.6 Models for Explaining Pore Nucleation Mechanism

There are different models that propose the theory behind the pore nucleation mechanism and the origin of pore nuclei. The first model explains local chemical dissolution at the electrolyte-oxide interface due to the applied electric field as the reason for pore nucleation. As mentioned, for electrolytes having pH greater than 5, the production of the barrier layer doesn’t allow the Al\(^{3+}\) ions to pass into the electrolyte solution. However, for electrolytes with a lower pH, the significant flow of Al\(^{3+}\) ions from the metal surface causes instability into the oxide-electrolyte interface. This regional instability thus produces changes in the applied electric field resulting in increased dissolution rate. This dissolution produces hemispherical depressions per cm\(^2\) in the metal-oxide and oxide-electrolyte interface, which results in the pore density. The electric field in the hemispherical depressions tends to be more due to their shape, which in turn increases the dissolution rate. Figure 2.6 represents the pore formation mechanism by the local dissolution of aluminum\[43\].

Another model proposed by Patermarkis et al. [43] mentions re-crystallization of the unstable rare lattice of oxide formed at the surface of aluminum to a more stable and denser nano-crystalline oxide. This re-crystallization and difference in density of the lattices produces a rupture in the surface, initiating the formation of pores.

The growth of pores begins with oscillations in the metal-oxide and oxide-electrolyte interface. The local electric field is amplified by the combination of these oscillations. The stable and unstable oscillations on the oxide layer causes changes in the topography of the oxide layer and forms pores of particular separation, which depends primarily on the pH of the electrolyte and the applied voltage. After pores nucleate, they undergo transient acceleration attaining a constant speed and shape.
2.7 Hexagonal Self Ordering

The porous assembly formed in the aluminum substrate attains a hexagonal ordering at certain steady state conditions when a certain electrolyte is used. Figure 2.7 represents the hexagonal ordering of pores and the cylindrical growth alongside the length [50]. This self ordering is possible due to the inter-pore force acting during the inception stage of the pores and the steady state growth conditions. Due to competitive ordering at the hexagonal domain edges, these hexagonal pores continue to expand. There is a lateral force present in between the pores that maintains the differences in alignment of two adjacent domains.

Few authors have proposed the structural-geometrical theory for explaining the hexagonal self ordering of the pores, which increases in regularity with increasing depth. In order to maintain an equilibrium for electric field distribution, the pore bases automatically arrange and level themselves resulting in the hexagonal order.

The inter-facial stress model explains that the inter-pore force is linked with the stress generated at the metal-oxide interface. After oxidation, the atomic density of aluminum in alumina is lower than aluminum by a factor of 2. This means that the volume of the anodized alumina increases about twice that of the original volume. This volumetric
expansion is the cause for stress generation during oxide formation at the metal-oxide interface, which contributes to the hemispherical shape of the pore base.

2.8 Factors Controlling the Self Ordering of Hexagonal Pores

2.8.1 Effect of Acid Type and Concentration

Weak or neutral solutions having pH greater than 5 form a flat nonporous aluminum oxide layer known as the barrier layer; hence, using solutions with pH less than 4 is important for formation of porous alumina layer. The type of electrolyte selected should be used under particular conditions for effective results. The conductivity and pH value of the electrolyte determines the amount of voltage to be used for the anodization. For example, anodization is carried out at low potential ranges for sulfuric acid (5V to 40V),
medium potential ranges (30V to 120V), and higher potential ranges for phosphoric acid (80V to 200V). The potential mismatch may cause the oxide layer to break down.

2.8.2 Effect of Anodizing Voltage

Anodizing voltage is the voltage applied between the two electrodes of the anodizing chamber. The pore diameter and barrier layer thickness are dependent on the applied voltage, and only a specific voltage must be used to obtain ordered arrangement of pores. O’ Sullivan et al. [46] proposed a model that showed a linear relationship between the pore diameter and anodization voltage, which is shown in Figure 2.8.

![Figure 2.8: Cell diameter versus anodizing voltage for different acids used during anodization [46].](image)

2.8.3 Effect of Temperature

The temperature of the anodization chamber should be kept lower than the room temperature in order to prevent the dissolution of the oxide formed in the acidic electrolyte. At room temperature, the bottom of the pores might get heated resulting in an
unequal electric field distribution that causes breakdown of the oxide. High temperature also results in the formation of cracks and holes in the oxide. On the other hand, extreme cooling of the electrolyte solution may result in freezing of the solution producing no results. Also, the growth of the porous layer is equally affected by temperature; lower temperature retards the growth of the porous oxide. Hence, temperature should be maintained in order to obtain the self-ordering of the pores.
3 EXPERIMENTAL TECHNIQUES

3.1 First Step Anodization

The process of anodization leads to the formation of a porous alumina film on the aluminum foil surface. Anodization takes place in an anodization chamber as shown in Figure 3.1 with the application of a suitable voltage and temperature conditions [51].

![Figure 3.1: Typical anodization setup for porous alumina formation.](image)

The electrolytic cell is a flat commercial cell with an attached platinum mesh as one of the electrodes, Ag-AgCl as the reference electrode, and a screw-lock system for attaching the aluminum foil for exposing it to the electrolytic solution. For anodization, the aluminum foil acts as the anode, and the platinum mesh acts as the cathode. A regulated power supply is used for providing a constant DC voltage as the anodization voltage. Three different electrolytes were used in our experimental technique: 0.3 M oxalic acid, 0.3 M sulfuric acid and 0.1 M phosphoric acid. Different anodization voltages were used for all three types of acids. Depending on the concentration and type of electrolyte, the
size and density of pores vary significantly. Figure 3.2 represents the laboratory equipment used for anodization experiment.

![Figure 3.2: Setup used in the laboratory for anodization of aluminum.](image)

**Table 3.1: Different types of acids used during the first step anodization process.**

<table>
<thead>
<tr>
<th>Acid Type</th>
<th>Concentration of Acid (M)</th>
<th>Applied Voltage (V)</th>
<th>Temperature Maintained (°C)</th>
<th>Time duration (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalic</td>
<td>0.3</td>
<td>45</td>
<td>~ at 4</td>
<td>15</td>
</tr>
<tr>
<td>Sulfuric</td>
<td>0.3</td>
<td>18</td>
<td>~ at 4</td>
<td>15</td>
</tr>
<tr>
<td>Phosphoric</td>
<td>0.1</td>
<td>160</td>
<td>~ at 4</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 3.1 represents the different concentration of acids used as electrolytes, the operating voltages, the temperature maintained and the time of anodization for performing
the experiment. These acids were chosen on the basis of their excessive use in literature owing to their ease of preparation, abundance in supply, and less hazardous nature.

The anodization chamber was placed on a heater and magnetic stirring stimulator from Fisher Scientific. A magnetic stirrer was placed inside the anodization chamber. The stimulator was used to stir the magnetic stirrer which in turn stirred the electrolyte inside the chamber in order to keep the reaction active.

The electropolished aluminum foils were attached to the anode on a metal plate which was attached to the screw. The screw can then be tightened until it reaches the hole in the chamber. The screw was tightened such that there are no leakages, and the foil was exposed to the electrolyte. The level of electrolyte filled the chamber till it covered the hole completely. The hole was circular in shape, and the aluminum foil that is exposed through the hole came in contact with the electrolyte solution and was anodized.

The anodization chamber was placed inside an ice box or thermos bucket along with small blocks of ice covering the entire anodization chamber. This was done in order to maintain the temperature of the anodization cell at around 0°C.

The anodization process mainly involved two different mechanisms as explained in detail: the formation of the alumina layer on the metal-oxide interface, and the lateral forces of repulsion between the adjacent pores in order to maintain the hexagonal self ordered assembly of the pores.

3.2 Chemical Etching of Alumina

Alumina membranes can be manufactured by a one-step, two-step or three-step anodization process. Due to the random nature of the pore nucleation mechanism in the first step anodization, it becomes evident that in order to create an idealized pore array, further ordering of the pores is required. Long range ordering is not present in the structures created by one-step anodization, although short range ordering is present.
Chemical etching is an intermittent step between the two anodization processes that increases the regularity and arrangement of pores significantly.

In the first step, anodization was carried out to form an ordered array of pores at the metal-oxide interface. The oxide layer was then removed that created indentions or "dimples" in the aluminum substrate. These indentations were the initiation sites for the formation of pores in the second step anodization. Hence, the pores do not nucleate randomly, and have a fixed area to originate. This chemical etching was carried out using a solution mixture containing phosphoric acid (6 wt%) and chromic acid (1.8 wt%) at a temperature of around 60 °C - 80 °C.

After the first step of anodization, the aluminum foil was carefully washed and dipped in the mixture, also known as the "strip-off" solution. The time for this wet etching process was usually maintained constant around 30 minutes at about 60 °C to 80 °C. The conventional laboratory oven was used for this process. The chemical etching time was usually double than that of the first step anodization time.

3.3 Multi-step Anodization

Porous membranes, after only one step of anodization do not yield a highly ordered array of pores. In order to use the porous membrane as a template for electrodeposition, it is very important to attain an ordered arrangement of nanopores. In our experiment, we have performed two and three step anodizations. However, not much of a difference was observed between two and three step anodization processes. The anodization conditions for any anodization process should be kept the same, otherwise it results in a different pore profile and arrangement.

For the second step anodization, the concentration of acids used were the same. However, the timings were varied for all the three different acids. Since the first step anodization was performed for 15 minutes, the second step anodization is usually
performed twice as long than the first step anodization. Table 3.2 represents the different concentration of acids used as electrolytes, the operating voltages, the temperature maintained and the time of anodization for performing the second step anodization. Since we already have the framework for the pore growth and arrangement, performing the second step anodization for longer times usually results in an ordered pores arrangement with high aspect ratio of pores.

Table 3.2: Different types and concentration of acid used during the second step anodization process.

<table>
<thead>
<tr>
<th>Acid type</th>
<th>Concentration of acid (M)</th>
<th>Applied Voltage (V)</th>
<th>Temperature maintained (°C)</th>
<th>Time duration (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalic</td>
<td>0.3</td>
<td>45</td>
<td>~ at 4</td>
<td>30</td>
</tr>
<tr>
<td>Sulfuric</td>
<td>0.3</td>
<td>18</td>
<td>~ at 4</td>
<td>30</td>
</tr>
<tr>
<td>Phosphoric</td>
<td>0.1</td>
<td>160</td>
<td>~ at 4</td>
<td>30</td>
</tr>
</tbody>
</table>

3.4 Post Treatment of Anodic Alumina

3.4.1 Pore Widening

Pore widening is also a wet chemical etching technique that is performed after the anodizations steps. It is a technique that is required in order to open the bottom of the pores and widen them from the bottom for enhanced electrodeposition. The difference between a sample without pore widening and with pore widening is illustrated in Figure 3.3 [52]. It is a final attempt to expand the pores as much as the surface can withstand so that they reach their maximum value. The pore bottom needs to be open for the ease of metal electrodeposition.
In the laboratory, 0.1 M phosphoric acid was used as the pore widening solution. Phosphoric acid is considered to be one of the best solvents for this process. It was observed that phosphoric acid yields relatively higher volume expansions, and wider pores are obtained. The pore widening times were varied. The two different pore widening times that were used were 30 minutes at 60 °C and 90 minutes at room temperature. The pore widening times were not fixed, and they depended on the nature and complexity of the pores. Depending on the pore size after characterizing the sample, the pore widening times were varied accordingly. The pore widening of 30 minutes at 60 °C, and 90 minutes at room temperature were compared to be same after characterizing the samples. However, it is very important not to exceed the pore widening times, as it results in collapsing of the pores by thinning down the walls excessively.

3.5 Electrodeposition

Electrochemically fabricated anodic alumina films were used as a template for electrodeposition of gold, silver and platinum nanowires. The solutions used for electrodeposition along with the applied voltage and duration are represented in Table 3.3.
Depending on the diameter of the gold particles, its color can change from red to purple and blue. The changes in the colors are mainly due to shape-defined changes in the plasmon resonance band of the gold nanoparticles. This band corresponds to the wavelength of light inducing the largest electric field on the exposed nanoparticles [49]. Noble metals like gold, silver and platinum were chosen for the electrodeposition process due to the fact that nanoparticles of noble metals can absorb light due to Localized Surface Plasmon Resonance (LSPR) and the resonance wavelength increases with an increasing dielectric constant. These nanowires can therefore be applied to chemical and bioanalysis as LSPR sensors [53]. Electrodeposition of metallic nanowires can be performed with a constant voltage source (potentiostatic) or constant current source (amperostatic).

For electrodeposition in the case of gold and silver, the temperature was maintained above the room temperature in order to aid the reaction. In the case of platinum, the electrodeposition setup was maintained at room temperature.

Figure 3.4: Electrodeposition setup including the electrodeposition chamber, magnetic stirrer/ heater and the potentiostat/galvanostat.
Table 3.3: Electrodeposition solutions used for the deposition of Au, Ag, and Pt and the different voltage conditions.

<table>
<thead>
<tr>
<th>Type of metal</th>
<th>Electrodeposition solution</th>
<th>Voltage/Current applied</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>OROTEMP 24 (commercial name)</td>
<td>-0.9 V</td>
<td>10–19 min.</td>
</tr>
<tr>
<td>Silver</td>
<td>1025 RTU (commercial name)</td>
<td>0.05 µA - 1µA</td>
<td>30sec–2min</td>
</tr>
</tbody>
</table>
| Platinum      | i) 5.0 mM Chloroplatinic acid and 0.1 M Hydrochloric acid in the ratio 1:1  
               | ii) 5mM chloroplatinic acid and 30 gm/L of boric acid in the ratio 1:4 | Varying AC or DC | Varying |

Electrodeposition is carried out in the same setup and equipment as anodization that is represented in Figure 3.4. Aluminum foil was wrapped around the electrodeposition chamber (cell) as shown in Figure 3.5, and a few metal pieces were placed beneath the cylindrical glass surface in order to maintain good contact of the electrolytic solution with the heater/magnetic stirring stimulator. The magnetic stirrer/heater is from Fisher Scientific. The temperature was maintained at around 90 °C for about 30 minutes.

The cathode is connected to the aluminum foil and tightened in the same manner and alignment as the anodization step. The alignment should be matched in order to use the maximum surface area for deposition. The orifice should be properly aligned to the area
exposed during anodization for maximum coverage. The anode is connected to the platinum mesh in this case. The reference electrode is connected to the Ag-AgCl electrode of the chamber.

The Intertech Systems voltage/current source was used as the power supply and an effective equipment that could be used both as potentiostat and amperostat.

Electrodeposition as shown in Figure 3.6, occurs at the surface of electrodes, and the targeted materials takes the free space of the template to form the required 1D morphologies [54]. The free space in our template is the pores, and hence the deposition takes place inside the pores. The duration of electrodeposition determines the length of the nanowires.

During electrodeposition, we monitor the current in the case of constant voltage deposition and the voltage in terms of constant current deposition. The sudden rise in current or the sudden decline in current gives an indication that the growth of nanowires has increased significantly, and the process needs to be terminated in order to prevent the excessive growth of nanowires and avoid the collapsing of the pore walls due to excessive
growth pressure. The entire process of anodic alumina membrane formation followed by pore widening and electrodeposition is represented in Figure 3.7.

After electrodeposition, the sample was cleaned using deionized water and was prepared for characterization.

3.6 Characterization of the Performance and Properties of Nanostructures

Technology at nanoscale has become one of the most challenging tasks for the scientific world to unveil. Groups from different areas of material science, bio-sciences, physics, and chemical engineering work in close collaboration with nanoscopy tools as it is very important to characterize the structural, chemical, and morphological properties of the nanostructures, in order to understand their chemical and physical properties, and be able to manipulate them at the atomic scale.
Imaging and analysis of nanostructures is an important part of any nanotechnology research. Researchers are now equipped with various advanced technologies for analyzing the objects at nanoscale. After the invention of the revolutionary equipment, Scanning Tunnelling Microscope, the nano-world took a new turn, and it made it possible to analyze the nanostructures, understand their composition, and manipulate them.

Different techniques and equipment are available for characterization of nanomaterials with specific properties and applications as per the requirements. Some of the commonly used characterization techniques are: Scanning Tunneling Microscopy (STM), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), X-Ray Diffraction (XRD) and so on. This
section gives an overview of the characterization techniques that were used during the research.

3.6.1 Atomic Force Microscope

Atomic force microscopy (AFM) is one of the many microscopy techniques that come under Scanning Probe Microscopy (SPM). SPM are a broad group of instruments that image and measure the properties of material, biological and chemical surfaces [55]. SPM works on the principle of scanning a sharp tip/probe across a surface, and measuring the sample-tip interactions to form an image. As mentioned earlier, the first of SPM techniques was Scanning Tunneling Microscopy (STM), which was developed by Binning and Rohrer, in the year 1982 at IBM in Zurich for which they were awarded with a Nobel Prize in 1986 [55].

When Binning, Quate, and Gerber developed the AFM in 1985, it consisted of a diamond shard attached to a gold foil. The diamond tip scanned the surfaces providing the interatomic van der Waals forces by the interaction mechanism [56].

Atomic Force Microscope as shown in Figure 3.8 consists of a cantilever, which is usually made up of silicon or silicon nitride with a probe mounted at the end. A piezoelectric device raster scans the surface beneath the probe. When the tip/probe comes close to the surface, due to the attractive or repulsive forces that build up it produces a deflection in the cantilever. The bending of the cantilever, which is as small as 0.01 nm, is detected by a laser beam, which is focused on the back of the cantilever. This laser beam is then reflected towards the sensitive photodetector. Due to the deflection of the beam, its position on the photodetector changes which is then converted into electrical signals to generate an image. AFM makes measurements in the x, y, and z direction by feedback mechanism that makes it easier to visualize the surface in three dimensions [55, 56].
feedback loop and the piezoelectric scanners control the motion of the probe. The deflection is measured by the "beam bounce method".

There are three principle modes of operation of the AFM. The contact mode maintains a constant cantilever deflection by using the feedback loops i.e. the force between the sample and the probe remains constant. The repulsive forces dominate the tip-sample interaction. In the non-contact mode, the tip does not come in contact with the sample, and the cantilever is oscillated with its resonant frequency. The attractive van der Waals forces tend to decrease the frequency of the cantilever, which in combination with a feedback loop system measures the tip to sample distance to construct a topographic image of the sample surface. In the tapping mode, the probe taps on the surface during scans, and by maintaining a constant oscillation amplitude, an image of the surface is
Figure 3.9: Plot of force as a function of probe-sample interaction in the different modes of AFM [57].

obtained. The force-distance curve is shown in Figure 3.9, which demonstrates the attractive and repulsive forces acting on the probe during different modes [57].

Figure 3.10: Complete setup of the AFM Agilent 5500 LS.
The AFM used in the research was from Agilent and the model number was 5500 LS. The picture of the AFM used in the research is shown in Figure 3.10. The AFM was used in order to analyze the pore geometry, pore alignment, and pore distribution. The pore size, and hexagonal arrangement of pores were easier to visualize with the use of this microscope.

### 3.6.2 Scanning Electron Microscope

The scanning electron microscope (SEM) produces a largely magnified image by the use of electrons instead of the light beam [58]. The SEM usually consists of two columns: the electronic console, and the electron column. The electronic console consists of control knobs and switches for adjusting the brightness, magnification, focus, contrast and other

Figure 3.11: Schematic of the scanning electron microscope [58].
features. The electron column consists of an electron gun fitted with a tungsten filament cathode. The electron beam is generated under vacuum and is focused to a small diameter by various lenses. The lower portion of the electron column is called the specimen chamber, which also consists of the stage controls for x-y-z movement, 360° rotation and 90° tilt.

![SEM setup](image)

**Figure 3.12:** Complete setup of the SEM from the manufacturer JEOL - JSM.6400.

The electrons generated from the electron gun are accelerated towards the anode and the condenser lens, which focuses the electron beam to a minimum focal point. The chamber should be maintained at a very high vacuum level of a minimum of $5 \times 10^{-5}$ Torr in order to maintain a dust-free and a clean environment for the column optics to operate. The vacuum prevents the oxidation, and burning of the hot tungsten filament at around 2700K [59].

The electron beam hits the sample, and it loses energy by random scattering and absorption. The detectors collect the back-scattered electrons, secondary electrons and x-rays to convert them into electrical signals and ultimately into pixels as output. A general representation of the procedure is shown in Figure 3.11 [58]. SEM was one of the
most important characterization instruments used in the research. The sample was characterized after every step in the SEM, which was from JEOL with the model number JSM 6400 (Figure 3.12). The pore size, pore assembly, general surface characteristics of the sample, and the growth of the gold, silver, and platinum nanowires were analyzed using the SEM.

3.6.3 Energy Dispersive Spectroscopy

The energy dispersive spectroscopy (EDS) system is usually integrated into SEM system, and is an accompanying elemental analysis technique used for the elemental analysis or chemical characterization of a sample [60].

Two basic types of x-rays [61] are produced by the inelastic interaction of the electron beam generated in the SEM with the specimen atoms. They are characteristic x-rays, which result from the ejection of inner shell electrons by the electrons, and continuum x-rays, which are produced by the interaction of beam electrons with the nucleus of specimen atoms.

The incident beam of electrons excites the electron from the inner shell of the sample due to which an electron hole is created. The outer energy shell electron tries to fill in the hole during which the x-rays are produced. This difference in energy, which is released in the form of x-ray, is detected by the EDS, and hence the elemental composition of the specimen is determined.

In the research, EDS was used for verification and characterization of platinum grown samples in nanoporous alumina membranes using oxalic acid. EDS was used for demonstration of the amount of platinum deposited in different areas of the sample.
4 Observations and Analysis

4.1 Oxalic Acid

Table 4.1: Anodization and intermediate conditions before electrodeposition on aluminum samples for oxalic acid.

<table>
<thead>
<tr>
<th>Process</th>
<th>Voltage (V)</th>
<th>Time (min)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First step anodization</td>
<td>45</td>
<td>15</td>
<td>~ maintained at 4</td>
</tr>
<tr>
<td>Dip stripping</td>
<td></td>
<td>30</td>
<td>60</td>
</tr>
<tr>
<td>Second step anodization</td>
<td>45</td>
<td>30</td>
<td>~ maintained at 4</td>
</tr>
<tr>
<td>Pore widening</td>
<td></td>
<td>90/30</td>
<td>34/60</td>
</tr>
</tbody>
</table>

Figure 4.1: Two step anodization with well-ordered arrangement of pores with the anodization conditions of 15 mins of first step anodization, 30 mins of chemical etching, 30 mins of second step anodization and 34 °C and 90 mins of pore widening observed under a) AFM and b) SEM.
The samples were observed after the anodization processes under the AFM and SEM, and presented in Figure 4.1. As shown in Figure 4.1a, the 3\( \mu \text{m} \times 3\mu \text{m} \) area scan of oxalic acid sample anodized under 15 mins of first step anodization, 30 mins of chemical etching, 30 mins of second step anodization and pore widening of 34\(^{0}\)C for 90 mins illustrates the dome shaped structure of hexagonally arranged pores. Each side of the hexagonal pore has a unique structure unlike a continuous pore circumference as expected. Figure 4.1b. is a top view of the template after two steps of anodization under similar conditions. As seen from the figure, on an average the pores measure around 90 - 100 nm. The pore sizes were measured by using AFM.

![Figure 4.2: Electrodeposition of Au nanowires on oxalic acid template under potentiostatic conditions with a voltage of -0.9 V for 12 mins.](image)

The hexagonal assembly of pores is an important part of the SEM analysis with oxalic acid. Pore widening of pores changes the size of the pores from 30 nm - 40 nm to about 70 nm -90 nm. The pore widening times determine the size of pores. The longer the
Figure 4.3: Au nanowires on three step anodized template with 15 mins first step anodization, 30 mins chemical etching, 15 mins second step anodization, 30 mins chemical etching and 30 mins of third step anodization.

Figure 4.4: Converging nanowires due to prolonged electrodeposition times.
pore widening time, the wider the pores. However, the pores stretch or thin down only up to a certain level after which they break down to yield no results.

After the anodization process, and post-treatment of the alumina with 0.1 M phosphoric acid solution to widen the pores for opening the pore bottom for electrodeposition, experiments were carried out with gold, silver and platinum nanowires in oxalic acid. Oxalic acid was chosen among the other acids due to the size of pores and the ease of seeing the results under the SEM.

Deposition of gold nanowires responded better with constant voltage conditions rather than constant current conditions. Hence, most of the Au deposition was carried out under constant voltage conditions. Figure 4.2 shows the growth and arrangement of nanowires in the oxalic acid template with nanowires emerging from the sides of the walls and attaining a hexagonal configuration. This arrangement of nanowires is also referred to as “nanocomb assembly”[62] in literature. The nanowires emerge as single wires from the sides of the pore bottom to give a definite hexagonal assembly. As seen in Figure 4.2, the pores underneath, and the emergence of nanowires is clearly visible on the central left corner.

The three step anodization process yields better arrangement of pores. The growth of Au nanowires in a three step anodized sample is shown in Figure 4.3. It shows individual nanowires originating from the pore walls and the hexagonal arrangement of pores is clear in the three step anodization process.

The length of the nanowires varies depending on the electrodeposition times. However, it doesn’t mean that we can grow them infinitely. After a certain time, they begin to converge. If the electrodeposition is continued for even longer, after converging they start to rip off the entire pores from underneath the template and collapse yielding no results.
Figure 4.4 is one such example of prolonged electrodeposition times on the oxalic acid sample. The nanowires begin to merge in different directions, and this force applied from the sidewalls of the pores creates an extra pressure on the pores, which ultimately leads to their collapse.

Electrodeposition of Au nanowires was followed by the deposition of Ag nanowires on the oxalic acid samples anodized under similar conditions with similar pore widening conditions and size of the pores. Figure 4.5 illustrates the growth of Ag nanowires with similar deposition patterns as Au. However, the Ag nanowire growth responded with constant current deposition rather than the constant voltage deposition. The sample shown in the Figure 4.5 was performed with a constant current of -0.1 uA for duration of 1 min.

There is a vast difference in the deposition times of the gold and silver nanowires. Silver nanowires grow much faster than gold and quickly cluster to form balls and plates. In contrast to the Au nanowire deposition, which is a slower process, Ag tends to be more
Figure 4.6: Platinum electrodeposition after pore widening of 35 °C for 90 mins and -0.55 V for 11 minutes from a mixture of H$_2$PtCl$_6$ and HCl in the ratio of 1:1.

Figure 4.7: a) Random distribution of platinum chunks along the surface of the pores. b) Decrease in platinum chunks alongside the surface of AAO moving from circumference to the centre.
agile with a growth rate almost 11 times higher than Au. This was observed in the laboratory after comparing the Au and Ag deposition timings under same conditions.

Another important observation in the regularity of the arrangement of nanowires is that they become more regularly arranged as we move towards the centre of the sample. Since the AAO template is formed in a circular pattern, the circumference of the template usually has a clustered arrangement of nanowires while the centre is more regular and almost indistinguishable from the original hexagonal arrangement of pores.

After Au and Ag, the third noble metal that was electrodeposited on AAO membrane formed by oxalic acid was platinum. The most important component for preparation of platinum electrodeposition solution was chloroplatinic acid ($\text{H}_2\text{PtCl}_6$). A mixture of 5 mM/L of $\text{H}_2\text{PtCl}_6$ and 0.1 M of Hydrochloric (HCl) acid in the ratio of 1:1 was used for initial testing. HCl was used as the supporting electrolyte.

![Image](image.png)

Figure 4.8: Platinum chunks magnified to show the texture. The electrodeposition was carried out by using 100 V peak-peak voltage, 100 Hz AC signal and -0.55 V DC offset voltage for 9 minutes.
Figure 4.9: Uneven distribution of platinum chunks on the surface on AAO membrane with DC electrodeposition conditions of -0.75V for 15 mins.

As seen in the Figure 4.6, the platinum deposits as chunk and not equal in diameter. The uniformly arranged hexagonal pores can be seen underneath the platinum chunks.

Platinum is deposited on the surface of the pores not in a random manner (Figure 4.7a.), but higher in concentration at the circumference, and then decreases as it moves towards the centre (Figure 4.7b.). Electrodeposition for platinum was performed under both D.C. and A.C. electrodeposition setups. D.C. electrodeposition was done using HCl as the supporting electrolyte; however, boric acid was used for both A.C. and D.C. electrodeposition setups.

AC and DC electrodeposition of platinum was done by using boric acid as a supplement to the choloplatinic acid solution. 30gms/L of boric acid and 5mM of H$_2$PtCl$_6$ was mixed in the ratio of 1:4. The results are shown in Figures 4.8 and 4.9.

Platinum electrodeposition performed by using both HCl and boric acid yielded almost similar results. The AC electrodeposition was in fact less productive than DC electrodeposition in case of boric acid.
Hence, the platinum electrodeposition yielded nanostructures in the form of platinum chunks rather than the usual nanocomb structure as observed in case of Au and Ag.

The EDS analysis was performed for platinum electrodeposition (Figure 4.10) to confirm the deposition of platinum and the amount of platinum deposited in different areas of the anodized sample. The larger peak represents the platinum concentration in three different areas of the sample and the smaller peak represents the aluminum concentration in the subsequent areas.

Figure 4.10: EDS analysis showing the platinum peaks.

The EDS analysis shows the type and concentration of the platinum deposited on the alumina substrate. We performed the EDS analysis of the sample at similar conditions of voltage, magnification and focus. This analysis was mainly to confirm the platinum deposition and the amount of platinum deposited at different parts in the sample.
The peaks in the figure illustrate the presence of platinum and the height of the peaks indicates the amount of platinum in three different regions of the sample starting from the circumference to the centre. It shows that the amount of platinum chunk decreases as we move towards the centre as indicated by the green, blue and red peaks. The presence of platinum was determined by the prestored values of energy in keV in the library of the program, which was then compared with the peak values obtained.

4.2 Sulfuric Acid

0.3 M of sulfuric acid was used for the first and second step of anodization. The anodization voltages and the pore sizes are different from the oxalic acid setup.

Table 4.2: Anodization and intermediate conditions before electrodeposition on aluminum samples for sulfuric acid.

<table>
<thead>
<tr>
<th>Process</th>
<th>Voltage (V)</th>
<th>Time (min)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First step anodization</td>
<td>18</td>
<td>15</td>
<td>~ maintained at 4</td>
</tr>
<tr>
<td>Dip stripping</td>
<td></td>
<td>30</td>
<td>60</td>
</tr>
<tr>
<td>Second step anodization</td>
<td>18</td>
<td>30</td>
<td>~ maintained at 4</td>
</tr>
<tr>
<td>Pore widening</td>
<td></td>
<td>varying</td>
<td>34/60</td>
</tr>
</tbody>
</table>

The anodization conditions and the post-treatment of alumina are as summarized in Table 4.2. The pore sizes in the sulfuric acid were in the range of 30 nm after pore widening, much smaller than the ones observed in oxalic acid template. The samples were observed after the anodization processes under the AFM and presented in Figure 4.11a and Figure 4.11b. As shown in Figure 4.11, the pore distribution is similar to that of oxalic acid scan differing only in the pore sizes.
Figure 4.12a gives an overview of the gold deposition with pores formed by sulfuric acid solution under similar anodization conditions as oxalic acid. The voltage in this case is much lower and so are the pore sizes. Similar patterns of Au nanowire deposition follow in the case of sulfuric acid with nanocomb structures. These nanocomb structures are more evident as we move towards the centre from the edges as seen in Figure 4.12b.

Figure 4.11: Two step anodization of aluminum sample with 0.3 M sulfuric acid under anodization conditions of 15 mins first step anodization, 30 mins chemical etching, 30 mins second step anodization and 34 °C and 90 mins of pore widening as observed under the AFM.

The pore widening times are significantly lower than that of oxalic acid samples. The pore widening times were decreased to 15 mins from the 30 mins for oxalic acid samples. Using the sulfuric acid sample if the pore widening was 30 mins, Au nanowires couldn’t be deposited as the pores collapsed completely.

A similar experiment for Ag nanowires growth was performed with a different set of conditions ranging from constant voltage to constant current.
Ag deposition at 30-40 nm pore sizes could not be attained as the agile growth nature of silver and the fast deposition completely rips apart the alumina layer exposing the template. The pore sizes could not be increased by increasing the pore widening timing as it pushed the pore walls to a limit that they completely collapse. Ag growth is almost ten times as fast as compared to Au growth, which makes it difficult to grow in small pore sizes. Ag electrodeposition forms cracks as shown in Figure 4.13 and Ag growth was concluded to be difficult for extremely small pore sizes.

4.3 Phosphoric Acid

0.1 M phosphoric acid was used as the electrolyte solution for the electrodeposition process. The pores obtained from phosphoric acid were larger than for oxalic and sulfuric acid. Table 4.3 gives an overview of the pore sizes in the anodic alumina template for different acid types after two step anodization process.
Figure 4.13: Attempts to deposit Ag nanowires on AAO template performed by using 0.3 M sulfuric acid.

Table 4.3: Comparison of pore sizes for different acids before and after pore widening.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Before Pore Widening (nm)</th>
<th>After Pore Widening (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalic acid</td>
<td>30-70</td>
<td>90-100</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>10-15</td>
<td>30-50</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>70-100</td>
<td>150-200</td>
</tr>
</tbody>
</table>

The pore sizes for phosphoric acid were in the order of 150 nm -200 nm.

Table 4.4 summarizes the conditions required for pre-deposition steps in phosphoric acid. Phosphoric acid had the best visibility due to the size of pores, and the light
Table 4.4: Anodization and intermediate conditions before electrodeposition on aluminum samples for phosphoric acid.

<table>
<thead>
<tr>
<th>Process</th>
<th>Voltage (V)</th>
<th>Time (min)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First step anodization</td>
<td>150</td>
<td>15</td>
<td>~ maintained at 4</td>
</tr>
<tr>
<td>Dip stripping</td>
<td></td>
<td>30</td>
<td>60</td>
</tr>
<tr>
<td>Second step anodization</td>
<td>150</td>
<td>30</td>
<td>~ maintained at 4</td>
</tr>
<tr>
<td>Pore widening</td>
<td></td>
<td>varying</td>
<td>34 / 60</td>
</tr>
</tbody>
</table>

refraction parameters. The area after anodization had a visible tint, which was visible to the naked eye. Figure 4.14 illustrates the pore geometry when the aluminum sample is anodized with phosphoric acid under 15 mins first step anodization, 30 mins chemical etching and 30 mins of second step anodization. It is not pore widened, and hence the pore arrangement is compact and the exact differentiated geometry of pores is not visible.

Figure 4.14: Pores on aluminum substrate grown with 0.1 M phosphoric acid under 15 mins of first step anodization, 30 mins chemical etching, 30 mins of second step anodization as observed under AFM.
Figure 4.15a represents the phosphoric acid pores without pore widening and Figure 4.15b represents the phosphoric acid pores with pore widening at 60°C for 30 mins. The 0.5 \mu m scale in figure b demonstrates the size of 2 pores and the pore wall is almost 500 nm averaging the pore size to be around 200 nm.

Figure 4.16 represents the pore distribution using phosphoric acid after two step anodization process.

Attempts were made to deposit Au nanowires on AAO template grown by phosphoric acid solution. The results or Au growth were inconclusive. There was no proof of Au nanowire growth. There were two possibilities, either the pore height was longer due to which pore widening was unable to open up the pores for electrodeposition or the pore sizes were becoming a hindrance in the deposition procedure. However, electrochemical
Figure 4.16: Pores on aluminum substrate grown with 0.1 M phosphoric acid under 15 mins of first step anodization, 30 mins chemical etching, 30 mins of second step anodization and 34 °C 60 mins of pore widening and b) Top view of the overall pore structure of phosphoric acid sample with two step anodization.

Sodium hydroxide (NaOH) etching techniques may be used to unplug the pores from the bottom for electrodeposition.
5 CONCLUDING REMARKS AND FUTURE CONSIDERATIONS

5.1 Conclusion

Our research focused on the laboratory techniques to process and synthesize aluminum substrates to form a nanoporous template for the production of nanowires. The focus of the research was to develop a simple yet efficient technique with minimum costs and maximum reproducibility for the production of noble metal nanowires. Different acids used for the process were based on an extensive literature search for the most convenient forms of electrolytes used for the development of anodic alumina pores. The three different acids used were 0.3 M oxalic acid, 0.3 M sulfuric acid, and 0.1 M phosphoric acid each of which had a unique set of characteristics, and played a crucial role in determining the shape and size of the alumina pores.

Anodization voltage and acid types are an important parameter in determining the nature of pores, which in turn decides the characteristic features of the nanowires produced. The production of nanowires is successfully carried out in similar electrochemical setup as the anodization process. The nanopores provide a base as the nanowires align themselves along the circumference of the hexagonally ordered pores and form a nanocomb arrangement as described earlier. Thus, we were able to produce vertically aligned nanometallic wires on a laboratory grown substrate.

The length of the nanowires determines the nanocomb assembly. After attaining a certain length, the nanowires begin to converge ripping apart the entire substrate due to the converging forces. We determined the importance of electrodeposition times for the proper nanocomb arrangement of the vertically growing metallic nanowires.

5.2 Future consideration

The field of nanowires is a very promising field because it has a lot of potential, and every single aspect of this research has something novel to explore. The optical properties
of the nanocomb assembly can be analyzed by the use of ellipsometer, and imaging ellipsometry can provide us with beneficial information about the thickness and refractive index of the structures. Energy Dispersive Spectroscopy (EDS) can be used on the samples for the determination of nature and elemental characterization of other unknown samples.

The noble metal nanowires show different colors due to the surface plasmon resonances after interaction with visible light. The conduction electrons have collective oscillations due to resonant excitation, which produces intense scattered light around wavelength of the resonant peak. This local field enhancement and strong scattering is useful for Surface Enhanced Raman Scattering (SERS), optical waveguides, and biosensors. This property can be utilized in analyzing the nature of molecules or atoms on the surface of porous membranes.

The synthesis of Au and Ag nanowires opens a whole world of possibilities for exploring other noble metal nanowires that can be grown on such porous templates. Platinum, which did not attain the nanocomb structure, can be studied further using other supporting electrolytes and concentration of $\text{H}_2\text{PtCl}_6$. Other conditions of AC and DC electrodeposition can be varied accordingly to test the dependence of growth of platinum nanowires on the voltage and current conditions.

The nanoporous alumina template prepared as template for the electrodeposition of noble metal nanowires is itself significant due to their use as bio-interface and ease of fabrication. They are not only used as template structures but also as functional interfaces for controlled release of molecules. These nanoporous substrates are advantageous due to their increased stability in their pore sizes. Moreover, these nanoporous membranes can be used as support structures for lipid bilayers for monitoring the activity of membrane proteins [63]. Highly ordered porous alumina can be prepared by anodization processes followed by the selective removal of aluminum and alumina at the backside of the pores giving it a sieve like structure which can then be coated with thin gold layer. Further
coating it with organic compounds in order to make it hydrophobic allows for measuring single channel recordings of proteins [64].

One dimensional nanostructures, particularly nanowires, are important due to their unique advantage including high surface-to-volume ratio, enhanced electrochemical activity, and electron conducting abilities. Gold nanowires are becoming important due to their unique advantage as electrochemical biosensor due to its biocompatibility for proteins, and electron transport property. The gold nanowire array produced by electrochemical deposition results in a large electro-active surface area, which is much larger than the conventional gold electrode. This highly electro-active surface can therefore be used for enhanced sensitivity and for the loading of enzymes [65]. Development of glucose based diagnostic devices with low detection limits is an example of the usage of gold nanowires for the non-invasive detection of glucose in bodily fluids other than blood [66]. Electrochemical bio-sensing with gold nanowires can be aimed towards the detection of nucleic acids, which is an important technology for the diagnosis of genetic and infectious diseases. Similarly, platinum nanowire array can respond to glucose molecules at a low potential and with sensitivity 50 times greater than that of the conventional platinum electrode [67]. Hence, the use of these noble metal nanowires for the construction of biosensors presents the possibility of achieving new levels of sensitivity with single molecule measurements. These materials have great possibility in the field of bio-sensing, with the generation of noble devices which can directly measure electric currents for the detection and characterization of single molecule changes.
REFERENCES

   http://www.nano.org.uk/what-is-nanotechnology


   no.5, pp. 22-36, 1960.


   nanotechnology,” in *Nanotechnology: Basic Science and Emerging Technologies*,

[7] E. Wolf and M. Medikonda, “Smaller is more, usually better, and sometimes entirely
   New!” , in *Understanding the Nanotechnology Revolution*, 1st ed.Weinheim,

   2006, pp. 89-95.

   the causes and consequences* [Online]. Available:
Available: http://crnano.org/whatis.htm


&group=nanoparticlesafety &module=2#content


