Model for porous alumina template formation

Raghunath Kanakala

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MODEL FOR POROUS ALUMINA TEMPLATE FORMATION

by

Raghunath Kanakala

Bachelor of Engineering
Andhra University, India
2001

A thesis submitted in partial fulfillment
of the requirements for the

Master of Science Degree in Electrical Engineering
Department of Electrical and Computer Engineering
Howard R. Hughes College of Engineering

Graduate College
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Entitled

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is approved in partial fulfillment of the requirements for the degree of

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Examination Committee Chair

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Examination Committee Member

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ABSTRACT

Model for Porous Alumina Template Formation

by

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Professor and Chair of Electrical and Computer Engineering
University of Nevada, Las Vegas

Anodized alumina templates have emerged as an important material system for the low cost fabrication of semiconductor and metal nanostructure arrays. This material system utilizes natural self-organization for the creation of periodic arrays of nanoscale structures. The underlying principle is that when aluminum is anodized in a suitable acidic electrolyte under controlled conditions, it oxidizes to form a hydrated aluminum oxide (alumina) containing a two dimensional hexagonal array of cylindrical pores. Due to the excellent periodicity of the pores, and the ability to control the pore diameters, such anodized alumina films can be used as templates for the fabrication of periodic arrays of nanostructures. A process-model based on underlying physics and chemistry of the anodization process is developed. The model developed unravels the interplay of various physical and chemical processes and their dependence on the process parameters such as the electrolyte, temperature, current and voltages and yields, an analytical solution relating the voltage (in constant current anodization) and current (in constant voltage anodization) to time. The predicted time behavior agrees fairly well with experimental
observations for sulfuric and oxalic acids. Thus, it is believed that the model is general enough and can be used for any anodization system with changes in appropriate model parameters.
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CHAPTER 1

INTRODUCTION

Semiconductor technology has advanced to the point where it is now possible to create devices incorporating one-dimensional confinement (quantum wells, or 2-D structures). Submicron lithography combined with production techniques such as Molecular Beam Epitaxy (MBE) and Metal Organic Chemical Vapor Deposition (MOCVD) is routinely used to fabricate quantum devices with novel characteristics [1].

A number of successful efforts have been reported, e.g., the fabrication of free standing Si or Si nano-wells or nano-pillars in this area of one- and zero-dimensional structures [1]. Semiconductor quantum wires and quantum dots, where electrons are confined in two and three dimensions respectively, can provide significant further enhancement of device performance [2]. In addition, these low dimension structures can emit and absorb light in an extremely narrow spectral range which can be controlled by the shape, size, composition, and doping of the nanostructure [2].

While the potential of semiconductor nanostructures is clear, their applications have been limited by the lack of a fabrication process suited to economic volume production. The common method of nanostructure fabrication uses electron-beam lithography to define the structures on a Molecular Beam Epitaxy (MBE) grown film which are then etched using Reactive Ion Etching (RIE) [2]. However, due to the serial nature of e-beam
lithography, this method is not suitable for the fabrication of large arrays of nanostructures needed for most practical applications. In addition, this technique has been shown to cause process related damage, which can significantly degrade device performance [2]. This has led to a number of successful fabrication techniques [2]. But these techniques seem to have approached their technological and economic limits, making the cost of controllably manufactured 1-D and 0-D structures prohibitively high as the dimensions of the individual structural units fall to the 10-100 nm range, especially when high density nano-arrays are needed [1].

A novel template based technology that is inexpensive, reliable and suitable for fabrication of large periodic arrays of semiconductor nanostructures, which is compatible with standard CMOS process is developed [3]. This technique uses material growth on a preformed template formed by electrochemical etching (anodization) of a thin film of aluminum deposited on an arbitrary substrate. Anodized alumina has been used as a nanotemplate for the implementation of number of metal and semiconductor nanostructures [4].

Expansion of anodic oxide film’s application fields increases the necessity of the detailed investigation of the film microstructures and mechanisms of their formation and modification [5]. When aluminum is anodized in a suitable oxidizing acid, a two-dimensional hexagonal lace work of quasi-periodic Al$_2$O$_3$ cells with uniform tubular pores, close-packed array of columnar hexagonal cells, with each containing a central pore normal to the substrate surface, is formed. The pore diameter and cell wall thickness depend on the anodization conditions such as the type and pH of the anodizing acid, anodization current/voltage, electrolyte temperature and the substrate conditions. These
values can be precisely controlled to form pore diameters between 4 and 100 nm [1,6,7]. Due to the excellent periodicity of these pores, and the ability to precisely control the pore diameters, anodized alumina films can act as ideal templates for the fabrication of periodic semiconductor nanostructures arrays [3].

While most of the work in this field has focused on bulk aluminum, the use of a bulk aluminum substrate precludes most photonic and electronic applications due to the opaque nature of the unconverted aluminum substrate, and the inability to readily integrate the nanostructure arrays with other device technologies. Therefore, direct creation of the template on the desired substrate is preferred, and thin film alumina templates are of particular importance for device applications. Even though the theoretical studies have resulted in some understanding of the growth mechanisms [1,6,7], there is no comprehensive model which captures the physics and chemistry of the process and has predictive capability.

The objective of this thesis is to develop physics and chemistry based comprehensive anodization model for process modeling of formation of porous alumina template. The specific contributions of this thesis are: (i) development of theoretical model based on the rate equation approach in which both the alumina formation and etching are considered (ii) development of a comprehensive model suitable for both cases of constant current and constant voltage anodization and electrolytes such as sulfuric acid and oxalic acid are considered.

1.1 Organization of the Thesis

In chapter 2, the literature review on the history of nanotechnology and the current thesis topic are discussed. In chapter 3, a detailed development and analysis of the
model proposed with respect to the constant current anodization with sulfuric acid and oxalic acid as electrolytes is discussed. Model analysis with respect to constant voltage anodization with sulfuric acid and oxalic acids as electrolytes is discussed in chapter 4. Conclusions and recommendations for future work related to this topic are presented in Chapter 5.
CHAPTER 2

LITERATURE REVIEW

Progress in information technology is often related to the ‘Moore’s law’, which predicts that the performance of semiconductor devices doubles roughly every 18-24 months. The increase in performance has been achieved mainly by shrinking the size of the individual transistors. Moore’s law has been valid for more than three decades and the semiconductor industry association believes that it will still be valid at least for one additional decade [8]. The trends towards continued miniaturization and the urge for increasing performance by even higher density of integration have directed R&D attention towards nanotechnology [9]. Nanotechnology has become one of the most important and exciting fields in physics, chemistry, biology, and engineering.

Establishing an understanding of the manufacturing methods at the building block level of matter is a historical opportunity in technology development. The ability to rearrange matter on a nanoscale is potentially a very economical way to obtain functionality with the promises of becoming the highest-added-value manufacturing approach. Nanoscale is a complex interdisciplinary playground. A nanoscale system requires time-dependent investigations of various simultaneous phenomena among a large number of components and scales [10].

There are eight main areas of interest in the field of nanotechnology, which are:
• Nanometrology
• Functional nanotechnology
• Nanomechanical devices and machines
• Molecular nanotechnology
• Particles, clusters and catalysis
• Nanostructured materials
• Extreme nanotechnology
• Nanofabrication

These areas are reviewed briefly below.

2.1 Nanometrology

This is a field of nanotechnology which deals with the measurement, testing, inspection and quality control methods. Development of these techniques for nanometrology is currently at an early stage. Various scanning probe microscopy techniques offer nondestructive surface characterization, but do not probe into the bulk of the material. Example of this type of characterization is atomic probe field ion microscopy or high resolution electron microscopy [11]. In these techniques, the sample is effectively destroyed during the process of examination in each case, and the process itself is rather slow.

Before the nanometrology can be routinely carried out on an industrial scale, there is a lot of work to be done in this field. The intention of industrial Nanometrology is to reduce measurements to a minimum, to save time and additional costs, but at the same time to ensure the produced work and high process stability through the measurement.
Based on the needs of the industry, the scientific demands on industrial nanometrology are reliability, comparability, and reproducibility. To reach these goals and hence more economic production, the research points of focus are:[12]

- Measurement instrumentation
- Calibration and calibration standards
- Tolerances and tolerability in the nanometer scale
- International measurement standards for nanometrology

The nanotechnology revolution critically depends on accurate and low-cost metrology in order to move nanodevices and systems out of research laboratories and into manufacturing. Economical manufacturing requires that the accuracy of the factory metrology tools be a small fraction of the smallest device feature size. Thus, nanosystems with \( \sim 10 \) nm features require dimensional metrology with accuracy \( \sim 1 \) nm. This is well beyond the capabilities of state of the art nanometrology [12].

The planar lithographic process that has underpinned the microelectronics industry depends on an accurate scale of lengths that is provided by the heterodyne laser interferometer. This technology is inadequate for the nanotechnology era and a new approach is needed. A new metrology paradigm is developed based on super-accurate optical encoder gratings written by a novel technique called scanning beam interface lithography (SBIL) [12].

2.2 Functional Nanotechnology

This term describes applications in which the nanostructures are used to produce improved optical, electronic or magnetic properties. Arrays of quantum dots are proving
to be highly efficient as lasers for optical communications purposes, with outstanding light efficiencies, low thermal heat dissipation and a wide range of available wavelengths. Nano-patterning of the oxide superconductors promises to improve magnetic flux pinning and the current carrying capacity. Quantum wires and single electron transistors are still in the developmental stage, which could revolutionize the way in which the integrated circuits are constructed [11]. Finally, nanomagnetic structures are already coming into use in high density information storage applications.

A timeline for development of functional nanotechnology could be as early as 10 years or as many as 50 years away. The general consensus, barring any unforeseen catastrophe, is that, functional nanotechnology will be developed within next 30 years. By functional it is meant working nanotech assemblers capable of creating dangerous virus like replications, more popularly know as ‘gray goo’.

2.3 Nanomechanical Devices and Machines

Another area with great potential is that of nanomechanical devices and machines. Micro machines and micro actuators are coming to in wide spread usage. For example, a micro accelerometer is found in every car airbag to trigger its operation [11]. The question is how far this technology will be transferred into the nanometer scale. Gearwheels, cogs, motors and actuators have been proposed that operate at the molecular level, but so far, most of these only exist as a computer simulation.

Lang et. al. [13] designed a chemically functionalized nano mechanical cantilever, which can be employed both as a versatile and also as an ultrasensitive detector for various gaseous analytes. The individual cantilevers are sensitized for the detection of the
analytes with the metal coatings. A chemical reaction takes place when the analyte molecules chemisorb or physisorb with the metal coating on the cantilever, producing an interfacial stress between analyte molecules and cantilever, resulting in a nanomechanical response (bending) of the cantilever. Using time-multiplexed optical beam-deflection technique, the bending is read out and thus, from the magnitude and temporal evolution of the bending, quantitative information on the analyte species and its concentration are derived. The micromechanical design of the sensor allows it to be seamlessly integrated into microelectronic devices. Its short response and high sensitivity over wide range of operating temperatures are added features.

Kawai [14] demonstrated DNA nanotechnology combined with MEMS technique. In this paper, single molecular imaging of DNA and its application to DNA electronic devices were presented. Kawaim states that the DNA is a molecule which has the ability of 'programmed self-assembly' and also has a "double helix structure with $\pi$-electron cores of well-stacking bases for one dimensional charge transport" [14]. DNA is a wide-gap semiconductor without the carrier doping and upon carrier doping of poly (dG).poly (dC) exhibits p-type behavior. The MEMS method coupled with nanolithography can give rise to an opportunity, to make a brain mimetic electronic circuit with the combination of DNA, various protein molecules and nanoparticles.

Fedder [15] proposed a MEMS design methodologies since the methodologies in wide use today, do not support the hierarchical representations that are suitable for the verification-based iterative design. An efficient way to design the integrated and complex MEMS is by structured design methodology, in which the cell hierarchy is propagated down to the lowest level of beams, plates and gaps. The proposed methodology will come
into wide usage once the supporting tools like layout synthesis and extraction are made commercially available.

2.4 Molecular Nanotechnology

Molecular nanotechnology is an area that is likely to have a much wider impact on our everyday lives. It refers to the technology for molecules sensing and molecular recognition. It is probably the most important field of nanotechnology at present, and seems destined to have the greatest impact because of its medical aspects. It is in this area that biology, physics, and engineering are coming together in a dramatic way [10].

One potential application of molecular nanotechnology is the integration of molecular electronics function with advanced silicon technology. One aspect of molecular electronics is the fabrication of devices whose function can be governed by single molecules. Though quite promising, these single molecule devices present new fundamental challenges [16]. At present, ultra high vacuum scanning tunneling microscope and other characterization tools are available to explore this field. Individual organic molecules are being isolated and characterized with STM [10].

Feedback controlled lithography (FCL) is a nanolithography technique used by Hersam [16] to generate arbitrary arrays of individual dangling bonds on the Si(100)-2X1:H surface. The surface is then doped with appropriately chosen organic molecules which will bind only at the desired sites of patterned dangling bonds. Since these dangling bonds serve as effective binding sites, molecules delivered in the gas phase to the surface self-assemble into the predefined patterns. Norbornadiene, copper phthalocyanine and C_{60} are the three different molecules for which the flexibility of self-
assembly technique has been demonstrated and studied by STM imaging and spectroscopy.

DNA nanotechnology is a promising field where the goals of nanotechnology are achieved in general. DNA is a polymeric molecule that contains the generic information of life. The key feature of DNA is its ability to recognize and associate with other DNA molecules by means of specific base pairing relationship [17]. DNA’s interaction specificity and the ability to form branched molecules represent a system whereby it is possible to gain large amounts of control over both linking and branching topology. The other advantages of DNA nanotechnology are that it does not require periodic matter which is the main reason for use of DNA in structural transitions to drive nanomechanical devices.

The idea behind DNA nanotechnology has been around since 1980. However, the realities of experimental practice have slowed the commercial realization of the technology. DNA is an extremely favorable construction medium. The key feature lacking previously in the construction of DNA is a rigid molecule. Seeman [17] discovered a new feature which has a key role in DNA construction, i.e., DNA double crossover molecule can be used as a rigid molecule. This feature is incorporated in building up DNA assemblies that use this rigidity in achieving control at the geometrical level, as well as on the topological level.

2.5 Particles, Clusters and Catalysis

This part of the nanotechnology field includes the understanding of properties and processes of nanoparticulate catalysts, modeling and catalyst fabrication. This is likely to
have a major impact in areas such as fuel production, materials production and environmental protection.

Apart from the medical related technologies, the controlled productions of the nanoparticles and clusters also have a substantial number of industrial and environmental applications, which are already exploited in remarkable ways [12]. The designer nanoparticle can be used from improving the sunscreens to better color phosphors for flat screen displays. Nanostructured catalysts have applications in the petroleum and chemical industries [11].

2.6 Nanostructured Materials

Nanomaterials are ubiquitous in occurrence in nature as well as in commercial technology. They present immense opportunities both for further fundamental understanding and exploitation technological applications [18]. The nanometer scale is expected to become a highly efficient length scale for manufacturing. Materials, with high performance, unique properties and functions, that traditional chemistry could not create, will be produced by nanotechnology [10].

Materials with nanoscopic dimensions not only have potential technological applications in areas such as device technology and drug delivery, but also are of fundamental interest in that the properties of a material can change in this regime of transition between the bulk and molecular scales.

Huezko [19] reviewed various template techniques suitable for fabrication of arrays of nanomaterials. Track-etch membranes, porous alumina, and other nanoporous structures are characterized as templates. Synthesis of carbon nanotubes has been
demonstrated in particular along with the polymeric nanostructures and nanometals. Various template synthetic techniques like electrochemical deposition, electroless (i.e. chemical) deposition, chemical polymerization, sol-gel deposition, chemical vapor deposition are dealt in detail. The termed template-synthesis approach utilizes the pores and channels in the nanoporous 'template' structures for forming the desired nanomaterial [19].

2.7 Extreme Nanotechnology

Area of extreme nanotechnology is where one deals with the atomic and molecular manipulation and assembly. One long term aim of such work is to produce computer memories of enormous densities. Another pure science objective is to study the properties through the bottom up approach, i.e., to assemble molecules piece by piece [2]. Atomic assemble method to produce macroscopic objects, even large items like airplanes and ships could be made out of this way.

A method that would allow doctors to tweak the innards of cells without even touching a patient's body is being developed in the U.S [20]. The technique is still in its infancy, and it is still not clear exactly what it does to the cells. But, initial experiments suggest that it might one day be possible to use the technique to treat cancer, speed up healing or even tackle obesity.

Ananthaswamy [20] study show that nanopulses can trigger cell suicide. The technique involves powerful electric fields with gradients of tens of megavolts per meter, applied for very short period of duration of the order of nano seconds. Applying electric pulses to cells is not new. In a technique called electroporation, electric fields that last
hundreds of microseconds are applied to cells. The voltage charges the lipid molecules in
the cell membrane, creating transient holes in the membrane. The method can be used to
get drugs or genes into cells. Teams led by Vernier, Karl Schoenbach of Old Dominion
University and Stephen Beebe of Eastern Virginia Medical School [20] have shown that
nanopulsing can kill tumor cells in culture. The pulses do not just fry cells, but lead to
changes such as the activation of enzymes called caspases, an early step in cell suicide.
These nanosecond-pulsed electric fields are too brief to generate an electric charge across
the outer membrane of cells, but they do affect structures within cells. So in near future,
we can expect a treatment for cancer with nanopulsing.

2.8 Nanofabrication

Nanofabrication is a field of nanotechnology in which structures of dimension less
than 0.1 micron meters are fabricated. Conventional methods like optical lithography
cannot be used because of the diffraction limits. Alternatives are ultraviolet or X-ray
lithography and electron or ion beam lithography processing, but more radical alternative
are required, especially for dimensions smaller than 10 nm. Scanning tunneling
microscope (STM) [11], the atomic force microscope (AFM) or scanning near field
optical microscope (SNOM) can be used to form patterns, which, in turn, can be used for
fabrication.

Alternatively, self-assembled techniques are also used in some cases to produce
regular patterns of molecules, especially in two-dimensional layers. Strands of DNA have
also been used as templates for the depositing of the inorganic compounds and filaments
like nanoparticles and nanowires. Parallel process, such as X-ray lithography, are

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inherently more attractive than serial process, such as focused ion beam machining, because of their higher throughput rates [11].

Atomic layer epitaxy (ALE) is a special modification of the chemical vapor deposition technique for depositing thin films and related surface structures [22]. A unique feature of ALE is its self-limiting growth mechanism which gives rise more attractive properties like accurate and simple film thickness control, sharp interfaces, uniformity over large areas, excellent conformality, good reproducibility multilayer processing capability and high qualities at relatively low temperatures [21]. In ALE, the reactant vapors are pulsed onto substrate alternately one at a time, and between the reactant pulses the reactor is purged with an inert gas. From the point of view of nanotechnology, the most important benefits of ALE are excellent conformality and easily realized sub-nanometer level accuracy in controlling film thicknesses [22].

Ritala et. al. [21] demonstrated a method of depositing thin films, using ALE. Two-dimensional confined quantum wires have been deposited by making use of a crystallographic selective ALE process. As a solution to chemical passivation of surfaces against ALE, is to react the active surface sites, such as hydroxyl groups, with a compound which would form new surface group inert to further reactions in the ALE process. The success of ALE in uniform modification in the inner layer of the nanoporous materials has been demonstrated experimentally.

Meschede et. al. [22] studied the requirements and potential application of the Atomic nanofabrication (ANF). ANF play's an important role in scientific and industrial applications where periodic structures play a vital role, where crystal growth of the
crystals is manipulated in all three dimensions. ANF is a technique for replacing optical lithography or any other nanofabrication method for mass production.

In future technological progress, scanning tunneling microscope (STM) and other scanned probe instruments play a significant role in manufacturing process in electronics, optics and precision machining. They require routine nanometer scale control over small sizes, surface morphology and electrical, chemical properties [23].

Dagata [23] reported his results on the STM pattern generation on the H-passivated silicon and AS-capped GaAs substrates. Analysis made on Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) and SEM reveals that the features consist of an oxide layer, approximately one to two monolayers thick. STS characterization and imaging of pn junctions were demonstrated and a novel system for performing STM-based lithography is described. Scanned probe concept is expected to be successful as a surface analytical instrument, in the technological arena.

Guarini et. al. [24] came up with a set of key processes for nano-meter-scale pattern transfer using a self-assembled polymer mask. These techniques have overcome the limitation of diblock copolymer film thickness, thermal stability and mask polarity. Thus, this process enables one to build a variety of silicon nanostructures. The simplicity, reproducibility and control over the self-assembly, combined with polymer compatibility with the silicon processing makes it a good tool for fabrication of silicon nanostructures.

2.8.1 Nanofabrication Using Self Assembled Alumina Templates

Fabricating nanostructures and tailoring their properties on scales less than 50 nm by conventional approaches are very challenging and costly. Such difficulties compelled researchers to seek alternative approaches and methods to produce nanostructures on
these length scales. A nonlithographic technique that utilizes highly ordered anodized aluminum oxide (AAO) porous membrane for low cost fabrication of semiconductor and metal nanostructure arrays is proposed [25]. For more than 40 years AAO has been the subject of various investigations. Homogeneous morphology of parallel pores is exhibited by the AAO, which can be grown perpendicular to the surface [26]. AAO is a mechanically robust material and is expected to increase the structure’s mechanical integrity making it more amenable to manufacturing processes [4].

When aluminum is anodized in a suitable acidic electrolyte under controlled conditions, it oxidizes to form anodized aluminum oxide containing a two-dimensional hexagonal array of cylindrical nanoscale pores [4]. The peculiar ‘native’ morphology of porous AAO of a honey comb film configuration has attracted great attention. The main features of the porous AAO films are: (1) uniform distribution of pores of diameter ranges from 10 nm to 400 nm; (2) ability to control the geometrical parameters of the AAO by changing the electrolyte composition and the processing parameters; and (3) high reproducibility on large scale samples [5].

The AAO template based nanofabrication approach is not material specific which provides another degree of freedom in engineering- namely fabrication of super lattices but of completely different materials and different internal structures [25].

Parkhutik and Shershulsky [27] developed a theoretical model for the porous structure formation based on the oxide growth at the oxide/electrolyte and oxide/aluminum interfaces. The features considered for the development of the model are: pore development as a result competition between the oxide growth and oxide dissolution, oxide dissolution by the electrochemical or electric field enhanced
mechanisms and three dimensional electric field distribution in the aluminum-oxide-electrolyte system. A system of 3 dimensional equations is developed to describe the pore formation. Analytical expressions for the pore size as function anodization parameters (voltage, temperature, and electrolyte pH) were developed. It is shown that pore size is dependent on the anodic voltage and the electrolyte pH.

Masuda and Hasegwa [28] experimentally demonstrated that an almost ideal ordered honey comb structure could be obtained in sulfuric acid solution. It was found that the potential required for self ordering is less in sulfuric acid than that for oxalic acid solution, permitting fabrication of ordered structure with smaller dimensions. An ordered structure could be formed only at the bottom of the film with the normal anodization procedure. Hence, they proposed a new approach for the symmetrical films with straight holes through out the entire film, a two-step anodization process. In two-step anodization, the concave texture of the Al surface which is formed after the first step (selective removal of the film after the first step of anodizing) is used as the initial stage for at the second step of anodizing, and an ordered pattern of pores even at the initial stages are obtained.

Jessensky et. al. [29] investigated the self-organized formation of ordered hexagonal structures in anodic alumina for both oxalic and sulfuric acid electrolytes and found that the size of the ordered domains depends strongly on the anodizing voltage. Using this effect, the current efficiency and the voltage dependence on the volume expansion of aluminum, during the oxide formation are correlated. Jessensky suggested that the mechanical stress induced due to the expansion of the aluminum during oxide
formation is the cause of the repulsive forces between neighboring pores during the oxidation process, which lead to self-organized formation of hexagonal pore arrays.

Vorobyova and Outkina [5] demonstrated a method of formation of functional layers as pillar microstructures based on aluminum anodic oxide films. Pillared microstructures by means of multistep anodization of Ta/Al film structure on ceramic and silicon (100) substrate are described. The depth-diameter ratio (aspect ratio) for the investigated composition was found to be 1.7-4.0. Two processes for the pillar growth through the porous $A_{l_2}O_3$ are proposed. The results indicate that the electrolyte composition could change the pillar size almost twice; the forming voltage influences the pillar height. When the electrochemical dissolution in the given electrolyte is known, the geometrical parameters of the pillar can be regulated.

Das and McGinnis [4] demonstrated the formation of porous silicon through the pores of an anodized alumina template on a silicon substrate. The alumina template acts as a protective coating on the porous silicon surface increasing its mechanical integrity, thus eliminating the necessity of the delicate handing required for these type of materials. It is also expected that the top coating protects the porous silicon from the environment and thus, reducing the aging effect and increasing the device life time. It is found that the porous silicon samples fabricated through the alumina templates show increased luminescence when compared to that of the porous silicon formed under identical condition without the alumina template.
CHAPTER 3

PHYSICS AND CHEMISTRY OF MODEL

3.1 Introduction

The nanoscale pores of anodized alumina templates are finding increasing applications in the fields of electronics, photonics and biochemical sensing. The ternary system ‘aluminum/anodic-oxide/electrolyte’ has been studied experimentally in details and significant empirical data have been accumulated relating to both barrier and porous alumina growth [3,5]. The pore diameter and the inter-pore spacing depend on the anodization conditions such as electrolyte pH, type of acid, anodization current/voltage, electrolyte temperature and the substrate parameters. The pore diameter can be varied between 4 to 100s of nm and the pore can be several microns deep [30-33]. Due to the excellent periodicity of the pores, and the ability to control the pore diameters, such anodized alumina films can be used as templates for the fabrication of periodic arrays of nanostructures [34]. The main features of porous Al anodic oxide films consists of the following: (1) a uniform distribution of microscopic pores of diameters in the submicrometer range; (2) arrangement of vertical straightforward pores at almost equal distance from each other; (3) an ability to control the geometrical processing regimes; and (4) high reproducibility of film structure properties for large-scale samples [4].
While most of the work in this field has focused on bulk aluminum, its use as substrate precludes most photonic and electronic applications due to the opaque nature of the unconverted aluminum substrate, and the inability to readily integrate the nanostructures arrays with other existing and mature device technologies. Therefore, direct creation of the template on the desired substrate is preferred. Thin film alumina templates are of particular importance for device applications. Such thin film templates formed on silicon substrates are of particular interest due to their promise for the integration of nanostructure with silicon electronic devices.

Even though numerous experimental data have been accumulated relating to porous alumina growth [27] which has resulted in some understanding of the growth mechanisms [2, 7, 35], the nature of the porous oxide growth is far from being understood. Several models have been proposed for the formation of porous oxide layers using different basic concepts. This study is focused on developing and using a rate equation model based on the physics and chemistry of the process for gaining a better understanding of the process. Ultimately, the model will be used as a predictive tool.

3.2 Experimental Procedure

P-type <100> 0.1-0.3 ohm-cm silicon wafers were first cleaned using a standard technique and etched in a 1% hydrofluoric acid solution to remove any native oxide. Next, a 0.5 μm thick aluminum layer was deposited on the back of the wafers and annealed at 450° C for 30 minutes to form a good electrical contact. Following this step, an aluminum layer (0.1 μm to 0.5 μm thick) was deposited by either sputtering or electron beam evaporation. In most cases, the samples were, then, annealed at 400° C for
30 minutes to ensure good adhesion. The top aluminum layers were then anodized in 2% sulfuric or 0.3M oxalic acid under constant voltage or constant current conditions. Constant voltage anodizations were performed at voltages in the range of 20 to 80V. Constant current anodization were erformed in the current range f 20 to 50 mA. The acid solution is circulated using a pump and chilled using a chiller to prevent heat buildup at the aluminum/electrolyte interface. During the anodization process, the voltage-time (constant current anodization) or current-time (constant voltage anodization) characteristics were monitored.

3.3 Model for the Anodization Processes

3.3.1 General Model

Porous oxide growth includes several stages that are easily detectable by monitoring the dependence of kinetic voltage (or current) on time or that can be directly observed by high-resolution electron microscopy. Immediately after switching on the anodic bias, a barrier oxide layer starts to grow (stage I). Relatively fine-featured pathways are, then, revealed in the outer regions of the barrier oxide prior to any true pore formation (stage II). Further anodizing results in the propagation of individual paths through the barrier oxide with their heads becoming enlarged (stage III). Finally, a steady-state pore structure is formed by closely packed cylindrical cells, each containing a pore at the center and separated from the aluminum metal by a layer of scalloped hemispherical barrier oxide (stage IV) [27]. The physics and chemistry of the formation and etching processes are shown in figure in Figure 3.1a and 3.1b.
3.3.2 Constant Current Anodization

From the experimental data of voltage versus time under constant current anodization, it is recognized that there are several phenomena included, which contribute to the measured potential difference. The measured voltage drop has three components, voltage drops at the cathode, in the electrolyte and at the anode. The anodic drop is a result of the anodic reactions, i.e. $\text{Al}_2\text{O}_3$ formation and etching. The initial linear increase in the voltage versus time plot shown in the Figure 3.2 is due to the setting up of electric field the cathode and in the electrolyte. For the modeling purposes this effect can be taken into account by shifting the plot by a constant voltage and a constant time. The voltage shift considered is the sum of voltage drop across cathode and electrolyte. This voltage drop depends on the current density. The voltage values of the shift as a function of current density are shown in Table I. In the case of sulfuric, the time shift was in the range of 3-5 seconds and the voltage shift was in the range 30 V. The shifting parameters for the voltage and time are specific to a particular anodizing system. The resulting voltage versus time curve after performing the shifts and normalization of the voltage data to the maximum potential difference, is shown in Figure 3.3.

The voltage-time characteristics can be explained based on the physics of the anodization and etching processes described below. It is noted that there are two distinct parts to the characteristics separated by $t^*$, the first linear increase (part I) and the exponential drop (part II). During part I, alumina formation by anodization of aluminum is controlled only by the kinetic rate of the reaction dictated by the electrolyte and anodization current. For a given current and electrolyte, the thickness of the alumina film increases linearly. This anodic drop is directly proportional to the resistance of the
alumina film. During part I of anodization, the thickness of the film increases and hence, its electrical resistance and the voltage drop across it, also increases. During part II of anodization, an array of pores develops on the alumina and the pore depth increase. The pore depth increase is due to larger rate of etching of alumina on the surface of the pore compared to the formation of alumina at the Al-alumina interface. In this case, the anodic voltage drop is dictated by the parallel resistances posed by the alumina in the pore and the non-pore area (pillar). The parallel resistance is controlled dominantly by the smaller of the two resistances, which, in this case, is the pore resistance. Since, during part II anodization the pore depth increases, i.e., the thickness of alumina in the pore area film decreases, the resistance and the anodic voltage drop decreases. But, the alumina under the pillar area continues to grow since etching reaction rate in this part of the film is smaller than the formation rate. The physics and chemistry of the formation and etching processes corresponding to part I and II are depicted in Figures 3.1a and 3.1b

3.3.3 Constant Voltage Anodization

It is recognized that the experimental data of the current versus time under constant anodization voltage includes several phenomena, which contribute to the measured current. As the current produced in the circuit is of low magnitude, a 1Ω resistor is placed in series with the circuit produced in the circuit and the voltage drop across the resistor is measured. The initial exponential drop in the current versus time plot shown in the Figure 3.4, is due to setting up of electric field at the cathode and in the electrolyte as discussed in section 3.3.1. For modeling purposes, this effect can be taken into account by shifting the voltages and time. The shifting parameters are specific to a particular anodizing system. An example of current versus time curve after the
elimination of this effect and normalization to the maximum current is shown in Figure 3.5.

3.4 Rate Equation Model

First, the physical model is qualitatively discussed, then a rate equation is developed for both the constant voltage and constant current cases. Analytical expressions for the thickness of the $\text{Al}_2\text{O}_3$ film in the pore and non-pore area are derived as a function of time.

3.4.1 Constant Current Anodization

Part I Anodization $t < t^*$

The rate of change of the $\text{Al}_2\text{O}_3$ film thickness with time can be written as a competition between the formation and etching processes and is given by:

$$\frac{dh}{dt} = \frac{K_{\text{form}}(I_o - hK)}{A} - \frac{hK}{A} K_{\text{etch}} \tag{3.1}$$

where the first term on the right hand side represents the formation and the second one the etching. In Equation 3.1, $h$ is the thickness of the $\text{Al}_2\text{O}_3$, $K_{\text{form}}$ is the rate constant of formation of $\text{Al}_2\text{O}_3$, $I_o$ is the current, $hK$ is portion of the current used of the etching process, $K_{\text{etch}}$ is the rate constant of the etching process and $A$ is the surface area of the anode. Note that in Equation 3.1, the current components used for the formation and the etching, add up to $I_o$. Integrating Equation 1 yields:

$$h(t) = \frac{K_{\text{form}}I_o}{K(K_{\text{form}} + K_{\text{etch}})} + Ce^{\frac{K}{A}(K_{\text{form}} + K_{\text{etch}})} \tag{3.2}$$

where $C$ is an integral constant. Using the initial condition that at $t = 0$, $h = 0$, $C$ can be obtained from Equation 3.2 to be:
\[
C = \frac{K_{\text{form}} I_o}{K(K_{\text{form}} + K_{\text{etch}})}
\]  \hspace{1cm} (3.3)

Substituting Equation (3.3) in Equation (3.2), \( h(t) \) can be written as:

\[
h(t) = \frac{K_{\text{form}} I_o}{K(K_{\text{form}} + K_{\text{etch}})} \left[ 1 - e^{-\frac{K_{\text{form}}}{A}(K_{\text{form}} + K_{\text{etch}})t} \right]
\]  \hspace{1cm} (3.4)

Part II Anodization \( t > t^* \)

The rate of evolution of the pore involves both etching and formation as described in section 3.3.1 and can be written as:

\[
\frac{dh_{po}}{dt} = \frac{K_{\text{form}}}{A} \left( I_o - h_{po}K \right) - \frac{h_{po}KK_{\text{etch}}}{A_{po}}
\]  \hspace{1cm} (3.5)

where \( h_{po} \) is the thickness of the pore in the formed \( \text{Al}_2\text{O}_3 \) film, \( K_{\text{form}} \) is the rate constant of formation, \( I_o \) is the applied current, \( K \) is a proportionality constant which describes the etching component of the current, \( K_{\text{etch}} \) the rate constant of etching, \( A \) is the surface area of the anode and \( A_{po} \) is the surface area of the pore.

Integrating Equation 3.5 yields:

\[
h_{po}(t) = \frac{K_{\text{form}} I_o}{AK_{po}} \left( \frac{K_{\text{form}}}{A} - \frac{K_{\text{etch}}}{A_{po}} \right) + Ce^{-\frac{K_{\text{form}}}{A}(K_{\text{form}} + K_{\text{etch}})}
\]  \hspace{1cm} (3.6)

where \( C \) is an integral constant. Using the initial conditions that at \( t = t^* \), \( h(t) = h_{po}(t) \), \( C \) can be shown to be:

\[
C = \frac{K_{\text{form}} I_o}{K_{po}(K_{\text{form}} + K_{\text{etch}})} \left( 1 - e^{-\frac{K_{\text{form}}}{A}(K_{\text{form}} + K_{\text{etch}})} \right) \frac{K_{\text{form}}}{K_{po}} \left( \frac{K_{\text{form}}}{A} - \frac{K_{\text{etch}}}{A_{po}} \right) e^{-\frac{K_{\text{form}}}{A}(K_{\text{form}} + K_{\text{etch}})}
\]

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Using the Equations (3.6) and (3.7), $h_{po}$ can be written as:

$$h_{po}(t) = \frac{K_{form} I_o}{AK_{po}} \left( 1 - e^{\frac{K_{form}}{A} \frac{K_{etch}}{\Lambda_{po}} (t - \tau)} \right) + \frac{K_{form} I_o}{K_{po} (K_{form} + K_{etch})} \left( 1 - e^{\frac{K_{form}}{A} (K_{form} + K_{etch}) t} \right) e^{\frac{K_{form}}{A} \frac{K_{etch}}{\Lambda_{po}} (t - \tau)}$$

(3.8)

The time evolution of the thickness of the $Al_2O_3$ film adjacent to the pores (pillar), $h_{pi}$, in part II can be written as:

$$\frac{d h_{pi}}{d t} = \frac{K_{form,pi}}{A} (I_o - h_{po}K_{po})$$

(3.9)

The $K_{form,pi}$ used in the Equation 3.9 is assumed to be $\sqrt[3]{2} K_{form}$. This assumption is valid because the growth under the pillar occurs by transfer of ions through a larger distance. Also, this $K_{form,pi}$ is an effective constant considering the effect of etching.

Note that in writing Equation 3.9, it is assumed that the etching of the pillar does not occur and formation of $Al_2O_3$ underneath the pillar at the $Al - Al_2O_3$ interface occurs using the ions transported through the pore and then laterally to the $Al - Al_2O_3$ interface underneath the pillar. Thus, the first term on the right hand side of Equation 3.5 is the same as the term on the right hand side of Equation 3.9.

Using $h_{po}(t)$ from Equation 3.8 in 3.9 and integrating yields:
\[ h_{p}(t) = \frac{K_{\text{form,pi}} I_{o}}{K_{p0} \left( K_{\text{form,pi}} + K_{\text{etch}} \right)} \left( 1 - e^{-\frac{K_{p0} t}{A} \left( K_{\text{form,pi}} + K_{\text{etch}} \right)^{t}} \right) + \frac{K_{\text{form,pi}} I_{o} (t - t^{*})}{A} - \frac{K_{\text{form,pi}} I_{o} (t - t^{*})}{A} \]

\[ \frac{K_{\text{form,pi}} I_{o}}{A^{2} \left( \frac{K_{\text{form,pi}}}{A} - \frac{K_{\text{etch}}}{A_{\text{po}}} \right)^{2}} \left( e^{-\frac{K_{p0} t}{A} \left( K_{\text{form,pi}} + K_{\text{etch}} \right)^{t}} - 1 \right) \]

\[ \frac{K_{\text{form,pi}} I_{o}}{AK_{p0} \left( K_{\text{form,pi}} + K_{\text{etch}} \right)} \left( 1 - e^{-\frac{K_{p0}}{A} \left( K_{\text{form,pi}} + K_{\text{etch}} \right)^{t}} \right) \left( e^{-\frac{K_{p0}}{A} \left( K_{\text{form,pi}} + K_{\text{etch}} \right)^{t}} - 1 \right) \]

(3.10)

3.4.2 Constant Voltage Anodization

The experimental current versus time curve such as the one shown in Figure 3.4 does not resemble the curve in the expected curve. The reason for this discrepancy is that the experimental curves do not exhibit stages III and IV. In stage I, \( Al_{2}O_{3} \) is formed by the constant supply ions. During very initial stages of growth since there is not much \( Al_{2}O_{3} \), etching that commence. During stage II, since there is a limited amount of \( Al_{2}O_{3} \), etching begins to occur. The rate of change of \( Al_{2}O_{3} \) film thickness, \( h \), with time, \( t \), can be written as a competition between the formation and etching processes and is given by:

\[ \frac{dh}{dt} = \frac{K_{\text{form}} \left( \frac{V_{o} A}{\rho h} - hK \right)}{A} - \frac{hK}{A} K_{\text{etch}} \]

(3.11)

where the first term on the RHS represents the formation of the film and the second one the etching. In Equation 3.11, \( V_{o} \) is the applied potential, \( K_{\text{form}} \) is the rate constant of the formation process, \( K_{\text{etch}} \) is the rate constant of the etching process, \( \rho \) is the resistivity of \( Al_{2}O_{3} \), and \( A \) is the surface area of the anode. The term within the parenthesis on the
RHS represents the portion of the current that is utilized for film formation and \( hK \) is the rest of the current used up for etching of the film. Note that the total current available for both these processes is given by \( (V_oA)/h \), where \( A \) is the resistivity of the Al₂O₃ film.

Integrating Equation 3.11 with respect to \( t \) yields, the following expression for the thickness of the film, \( h(t) \):

\[
h(t) = \frac{K_{form} V_o A^2}{K \rho (K_{form} + K_{etch})} \left( 1 - e^{-2K(t+c) \frac{(K_{form} + K_{etch})}{A}} \right)
\]  

(3.12)

where \( C \) is an integral constant. Using the initial condition that at \( t = 0, h = 0 \), the integral constant, \( C \) is found to be 0 and therefore, Equation 3.11 reduces to:

\[
h(t) = \frac{K_{form} V_o A^2}{K \rho (K_{form} + K_{etch})} \left( 1 - e^{-2K \frac{(K_{form} + K_{etch})}{A}} \right)
\]  

(3.13)

It is observed from Equation (3.13) that the film thickness changes as power half of a \( (1-e^{-t}) \).
CHAPTER 4

RESULTS AND DISCUSSION

4.1 Model Parameters for Constant Current Anodization

The experimental value of current density \( I_o \) of 20mA/cm\(^2\) with sulfuric acid as the electrolyte and anode surface area of 0.9018cm\(^2\) are employed in the calculations for obtaining the model parameters. The procedure for obtaining the model parameters is as follows. Given that \( I_o = 20mA/cm^2 \), \( A = 0.9018cm^2 \), and \( h = 300A^o \), and noting that \( hK \leq I_o \), equating \( hK \) to \( (I_o/12) \), yields:

\[
K_{\text{max}} = \frac{I_o}{h} \times \frac{1}{12} = \frac{20 \times 10^{-4}}{300 \times 10^{-10}} \times \frac{1}{12} = 5555
\]

At the time where the voltage reaches its peak value, i.e., \( t = t^* \) Figure 3.2, it is assumed that the voltage reaches 88% of its maximum value which implies that:

\[
1 - e^{-\frac{K}{A}(K_{\text{form}}+K_{\text{etch}})t^*} = 0.88
\]

Using Equation (4.2) and solving for \( K_{\text{form}} \) and \( K_{\text{etch}} \) with an assumption that

\[
K_{\text{etch}} = 0.45K_{\text{form}}
\]

yields:

\[
K_{\text{form}} = 5.2746 \times 10^{-09} \text{ m}^3/\text{sA} \text{ and } K_{\text{etch}} = 2.2735 \times 10^{-09} \text{ m}^3/\text{sA}
\]

All the fitted model parameters are listed in Table II. It is noted that these parameters are temperature and electrolyte dependent.
The $Al_2O_3$ thickness for the pillar was obtained by adding the results of Equation 3.4 for Part I with that of Equation 3.8 for Part II. Recognizing that the voltage across the anode is directly proportional to the thickness of the $Al_2O_3$ layer, given that the area of the anode and the current are constant, the computed thickness versus time and the experimental voltage versus time are similar, but on a different scale. Thus, normalizing both data such that the maximum value in each data set is 1.0, they can be plotted in the graph and compared. Normalized computed and experimental data are shown as a function of time in Figures 4.1 – 4.3 for various current densities. Note that the agreement between the results is very good to an error percentage of 2-5%. Thickness of $Al_2O_3$ pillar, $h_{po}(t)$, and pore, $h_{p}(t)$, were computed using Equations 3.8 and 3.10. $h_{po}(t)$ and $h_{p}(t)$ at 35 seconds are 347nm and 61nm respectively and the values agree with the experimental data with in 4%. The agreement can be brought to be within 1% by adjusting the model parameters.

$t^*$, the time which separates Part I and Part II of anodization discussed in chapter 3, varies with the current density. From the experimental data, it is found that the $t^*$ changes with current density inversely and is given by:

$$t^* = \frac{A}{i} + B$$

(4.4)

A is given by 75 and B is 1.5, these values are obtained after a lot of observations made on the experimental data. $t^*$ versus current density obtained from experiments along with the values computed using Equation 4.4 are shown in Figure 4.4. From Figure 4.4, it is observed that the higher current density, smaller is the $t^*$, which implies that the barrier
formation is faster for higher current density. This is consistent with the results reported in [35].

Plots of voltage versus time obtained using model solutions and parameters, with a ratio of $K$ to $K_{po}$ of 1 for various current densities are shown in Figure 4.5. Even though the general trends of Part I and Part II are similar, the values differ quantitatively for various current densities. The plots of voltage versus time obtained by the theoretical modeling utilizing the modeling parameters, with a ratio of $K$ to $K_{po}$ be 3 for various current densities are shown in Figure 4.6. Comparing the plots for the same current density but difference $K$ to $K_{po}$ ratio as shown in Figures 4.5 and 4.6, it is observed that the slope of the curve in the second part increases with the increase in the ratio of $K$ to $K_{po}$.

The model holds good for the 0.3M oxalic acid as the electrolyte with the same model parameters as the one used for sulfuric acid as the electrolyte. Normalized computed and experimental data are shown as a function of time in Figures 4.7 – 4.9 for various current densities. Note that the agreement between the results of the model are very good.

4.2 Model parameters for Constant Voltage Anodization

Experimental values of applied potential (V) of 50V with sulfuric acid as the electrolyte and anode surface area of $0.9018 \text{ cm}^2$, are employed in the calculations for obtaining the model parameters. The procedure for obtaining the model parameters is as follows. Given that $V_0=50\text{V}$, $A = 0.9018 \text{ cm}^2$, $h = 300 \text{ nm}$ and $\rho = 2\times10^{11} \text{ } \Omega\text{m}$, which is
the resistivity of $\text{Al}_2\text{O}_3$, and noting that $hK \leq \frac{V_n A}{\rho h}$ and equating $hK$ to $\frac{3}{4} \frac{V_n A}{\rho h}$ yields:

$$K = \frac{(50) \times 0.9018 \times 10^{-4}}{2 \times 10^{11} \times (300 \times 10^{-9})^3} \times \frac{3}{4} = 0.1878$$

(4.5)

The choice of $hK$ equal to $\frac{3}{4} \frac{V_n A}{\rho h}$ is made to fit the experimental data well and is kept the same for all the voltages. It is noted from the work on the constant current anodization reported in section 4.1 that $t^*$ is the value which separates the two distinct parts of the voltage versus time characteristics, the first linear increase and exponential drop. Here, it is assumed that $t^*$ is the value that separates the stages I and II which is usually taken to be 5s. To obtain values for $K_{\text{form}}$ and $K_{\text{etch}}$, experimental $h(t)$ attains 95% of its maximum value in a time, $t = t^*$, which in this case is 6 seconds. This implies that:

$$\sqrt{1 - e^{-\frac{2Kt^*}{A(K_{\text{form}} + K_{\text{etch}})}}} = 0.95$$

(4.6)

Using the equation 4.6 and solving for $K_{\text{form}}$ and $K_{\text{etch}}$ with assumption that $K_{\text{etch}} = 0.5 K_{\text{form}}$, yields:

$$K_{\text{form}} = 5.655 \times 10^{-05} \; ; \; K_{\text{etch}} = 2.827 \times 10^{-05}$$

(4.7)

All the fitted model parameters are listed in Table III. It’s noted that these parameters are temperature and electrolyte dependent.

The current in the external circuit is inversely proportional to the thickness of the $\text{Al}_2\text{O}_3$ layer, given the area and the applied voltages are constant. Therefore, it is expected that, the computed film thickness versus time and the experimental current

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versus time are similar, but on a different scale. Thus, normalizing both the data such that
the maximum value in each data set is 1.0, they can be plotted in the figure and
compared. Normalized computed and experimental data are shown as a function of time
in Figures 4.10-4.13 for various applied potential in the range of 20-75 V. Note that the
agreement between the theoretical and experimental results is very good for all the
voltages except for 75 V in which case, the agreement is fairly good. The discrepancy
between the data for 75 V case can be attributed to dependence of the model parameters
such as the initial shifts in time and current or any of the assumptions made in the
derivation of the parameters on the voltage itself. Height of Al₂O₃ pillar height computed
for the voltage range of 20-75 V after 15 seconds is in range of 3-4 nm. This is in good
agreement with the experimental data deduced from the growth rate from thicker films.
The model developed is complete for anodization with sulfuric acid and can be employed
for predictive purposes.

The stages III and IV are not observed in the experimental results since they take
place at times much longer than 20 seconds (time used for simulation) depending on the
conditions of the electrolyte and anodization. For instance, for an anodization at 80V, a
300 nm film undergoes the stages III and IV of anodization at 20sec. Additionally, our
model is focused on stages I and II and hence short times of anodization, does not include
stages III and IV due to lack of good experimental data.

For any other constant voltage anodization system with different electrodes or
electrolytes or conditions, the general formulation and predicted behaviors of \( h(t) \) and
current versus time, will stay the same, except that the model parameters and quantitative
values of current and \( h(t) \) will be different.
4.3 General Observations

- Agreement between the model and experimental results for both sulfuric acid (constant current and constant voltage) and oxalic acid (constant current) as electrolytes is within 4%.

- Our results show that the barrier layer thickness $h_{po}$ is a function of time. $h_{po}(t)$ reaches a maximum of 150 to 200 nm depending on the process conditions when the voltage reaches a peak, then decreases and reaches a constant value of thickness of 5 to 10 nm. This explains the observed experimental voltage versus time behavior.

- The above observation is somewhat in disagreement with models suggested in the literature [3, 28, 36]. This proposed model requires experimental verification by direct microstructural observation of varying $h_{po}$ with time through thickness analysis of the nanopores at varying times during growth.

- The model developed is complete for anodization with sulfuric acid and oxalic acid and can be employed for predictive purposes.

- If the concentration of the electrolyte (sulfuric acid or oxalic acid) is varied, it is expected that the model will not change, but the model parameters will change.

- The general relationships obtained for the sulfuric acid system, such as the $t^*$ dependence on current density is expected, apply to all other systems at least qualitatively. This needs experimental validation.
CHAPTER 5

RECOMMENDATIONS AND CONCLUSIONS

In this thesis, a theoretical model for porous structure formation during electrochemical anodization of aluminum is proposed based on the rate equation approach in which both the alumina formation and etching are considered. The model also, takes into account the process parameters such as potential difference, current density, and electrolytes, for the case of constant voltage anodization. Equations providing a general description of the porous alumina formation employing minimal number of parameters and yet capturing the essence of the experimental observations are developed and solved analytically. The results of normalized voltage versus time and normalized current versus time obtained from the model are in good agreement with the experimental results reported in the literature for a range of voltage, 20 – 50 mA for constant current anodization and 20-70 V for constant voltage anodization, with a deviation of 2-5 %. The agreement can be brought to be within 1% by adjusting the model parameters. The qualitative dependence of the behavior of process parameters such as potential, current density, and electrolytes will be applicable to all anodization systems. Also, the thickness of the alumina film obtained from the model at a particular time is in the range of 3-5nm from the experiments.
Recommendations:

- Develop relationship between model parameters and electrolyte conditions.
- Check the validity of the model for longer anodization times by compare with experimental data.
- Investigate the science of the pore formation and its relation to process conditions.
Table I. Shifting current (mA), voltage (V) and time (sec.) parameters used for sulfuric acid as electrolyte

<table>
<thead>
<tr>
<th>Current Density (mA)</th>
<th>Voltage shift (V)</th>
<th>Time Shift (sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 mA</td>
<td>28</td>
<td>3.4</td>
</tr>
<tr>
<td>30 mA</td>
<td>30</td>
<td>2.7</td>
</tr>
<tr>
<td>50 mA</td>
<td>70</td>
<td>3.4</td>
</tr>
</tbody>
</table>
Table II. Model parameters obtained by fitting the theoretical results to experimental results for a current density, $I_o = 20 \, mA$.

<table>
<thead>
<tr>
<th>Model Parameters</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proportionality Constant</td>
<td>$K$</td>
<td>5555</td>
<td>A/m</td>
</tr>
<tr>
<td>Rate constant of formation of $\text{Al}_2\text{O}_3$</td>
<td>$K_{\text{form}}$</td>
<td>$5.27462 \times 10^{-9}$</td>
<td>$m^3 / sA$</td>
</tr>
<tr>
<td>Rate constant of etching of $\text{Al}_2\text{O}_3$</td>
<td>$K_{\text{etch}}$</td>
<td>$2.3735 \times 10^{-9}$</td>
<td>$m^3 / sA$</td>
</tr>
<tr>
<td>Proportionality Constant in pore formation</td>
<td>$K_{po}$</td>
<td>16665</td>
<td>A/m</td>
</tr>
</tbody>
</table>
Table III

Fitted model parameters are listed for a voltage of 50V for sulfuric acid as the electrolyte

<table>
<thead>
<tr>
<th>Model Parameters</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proportionality Constant</td>
<td>$K$</td>
<td>0.1878</td>
<td>A/m.</td>
</tr>
<tr>
<td>Rate constant of formation of $Al_2O_3$</td>
<td>$K_{form}$</td>
<td>$5.655 \times 10^{-5}$</td>
<td>$m^3/\text{sec.A.}$</td>
</tr>
<tr>
<td>Rate constant of etching of $Al_2O_3$</td>
<td>$K_{etch}$</td>
<td>$2.827 \times 10^{-5}$</td>
<td>$m^3/\text{sec.A.}$</td>
</tr>
</tbody>
</table>
Figure 3.1: Schematic picture of (a) anodization and (b) pore formation $h_{pl}(t)$ and $h_{po}(t)$ are time dependent variables.
Figure 3.2: Experimental data of voltage versus time for a constant current of $I_0$ of 20mA

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Figure 3.3: Modified and normalized experimental data of voltage versus time for a current density of 20mA
Figure 3.4: Experimental data of current versus time for an applied potential of $V_o$ of 40V
Figure 3.5: Modified and normalized experimental data of current versus time for an applied potential difference of $V_o$ of 40V.
Figure 4.1. Theoretical and experimental data of voltage versus time for anodization at a current of $I_0$ of 20 mA.
Figure 4.2 Theoretical and experimental data of voltage versus time for anodization at a current of $I_0$ of 30 mA.
Figure 4.3. Theoretical and experimental data of voltage versus time for anodization at a current of $I_0$ of 50 mA.
Figure 4.4. Average experimental $t^*$ vs Current density (mA/cm$^2$) along with values computed from Equation 4.4.
Figure 4.5. Theoretical data of voltage versus time at 20 mA, 30 mA and 50 mA, respectively, for ratio of K to Kpo be 1.
Figure 4.6. Theoretical data of voltage versus time at 20 mA, 30 mA and 50 mA, respectively, for ratio of $K$ to $K_{po}$ be 3.
Figure 4.7. Theoretical and experimental data of voltage versus time for anodization at a current of $I_0$ of 45 mA.
Figure 4.8. Theoretical and experimental data of voltage versus time for anodization at a current of $I_0$ of 50 mA.
Figure 4.9. Theoretical and experimental data of voltage versus time for anodization at a current of $I_0$ of 55 mA.
Figure 4.10. Normalized experimental and calculated data of current versus time for anodization at an applied potential difference of 20V.
Figure 4.11. Normalized experimental and calculated data of current versus time for anodization at an applied potential difference of 40V.
Figure 4.12. Normalized experimental and calculated data of current versus time for anodization at an applied potential difference of 60V.
Figure 4.13. Normalized experimental and calculated data of current versus time for anodization at an applied potential difference of 75V.
REFERENCES


[28] Masuda and Hasegwa


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