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Electrochemical Synthesis and Structural Characterization of Titania Nanotubes

by

Que Anh S. Nguyen

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

 in

Materials Science and Engineering

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Thomas Devine, Chair Professor Ronald Gronsky Professor Rachel Segalman

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Electrochemical Synthesis and Structural Characterization of Titania Nanotubes

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Que Anh S. Nguyen

Abstract

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by

Que Anh S. Nguyen Doctor of Philosophy in Materials Science and Engineering

University of California, Berkeley

Professor Thomas Devine, Chair

Titania nanotubes have emerged as an exciting new material with a wide array of applications such as sensors, dye sensitized solar cells, and batteries due to their semi-conducting nature, high surface area, and distinct morphology. The nanotubes, synthesized electrochemically in a fluoride-containing electrolyte, are vertically aligned, close-packed, organized structures, with similar diameter and length. The formation mechanism responsible for the organized nanopore/nanotube arrays were examined by studying the effects of processing parameters (anodization voltage, synthesis time, electrolyte composition, substrate surface conditions, etc..) on the growth and structure of electrochemically synthesized titania. Characterization of the nanotubes crystal structure, morphology, and oxide composition were performed via cross-sectional and high-resolution transmission electron microscopy (TEM), micro x-ray diffraction (XRD), energy dispersive spectroscopy (EDS), and electron energy loss spectroscopy (EELS). Experimental results from the synthesis and characterization efforts lead to a novel planar-interface-breakdown model to describe the initiation of organized arrays of nanopores and nanotubes formed via anodization of titanium. It is proposed that the initiation step is triggered by compositional changes in the oxide and electrolyte, near the interface region, that break down the planar surface. In the electrolyte, the compositional changes are enhanced by ionic species, such as fluoride that form complexes with metal cations. In the oxide, the compositional gradient results from depletion of metal cations near the oxide/electrolyte interface. The proposed mechanism indicates that, in addition to the compositional gradient, the initiation of nanopores is controlled by the potential gradient in the oxide as well as the oxides dissolution rate. The initiation step is crucial not only for the growth processes that proceed during anodization, but also for the organization of the pores that result from synthesis. This mechanism, although formulated for the case of anodization of Ti, may be extended to other porous anodic oxide systems.

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Chapter 1

Introductory Remarks

Nanostructured metal-oxides have garnered great scientific interests due to their high surface area and size-dependent properties. Reducing surface features down to the nanometer scale can lead to material systems with new and unique physical, chemical, and electronic properties, which can offer considerable promise in improving current devices' performance or the development of novel applications. Examples of size-dependent properties run abound in the field of materials science. The most notable examples include the quantum confinement effect seen in CdS nanocrystals, which exhibit an increase in band gap energy with decreasing crystal size. [Alivisatos, 1996] With metal-oxides, having nanosized features can result in an enhanced exciton binding energy due to size confinement, or the presence of more defect levels in semiconductor materials due to the increased surface-to-volume ratio, as seen in ZnO nanorods and ZnO nanowires respectively. [Gu et al., 2004; Yang et al., 2002]

Among the most studied nanostructured metal-oxide systems are titania nanotubes, nanopores and nanowires. Due to its chemical stability, semiconducting properties (typically n-type), photocatalytic properties, and high-aspect ratios, titania nanostructures have potential in a wide variety of applications. They have been used as an electrode material in photocatalysis [Adachi et al., 2000], sensing [Traversa et al., 2000; Mor et al., 2004], water splitting [Shankar et al., 2009; Lin et al., 2003], and batteries [Fang et al., 2009; Kavan et al., 2004; Armstong et al., 2005]. These applications require the electrode to be in contact with either a gaseous, liquid, or solid electrolyte and thus the increase in surface area provided by the nanostructured oxide can have a large effect on the performance of the electrode.

Recently, particular focus has been placed on titania nanotubes and their implementation in solar cells devices. The semiconducting nanotubes are used as the electron transport material in dye sensitized solar cells [*Zhu et al.*, 2007; *Varghese et al.*, 2009], and hybrid organic/inorganic solar cells [*Yu*, 2009; *Shankar et al.*, 2007]. Dye sensitized solar cells, as developed by Graetzel, utilizes a nanoparticle network of titania [*Gratzel and Kalyanasundaram*, 1994]. It's been proposed that by substituting the titania nanotubes for the nanoparticles, higher efficiency cells could be developed due to the increase in electron transport facility provided by the tube morphology over the tortuous nanoparticle network. [Mor et al., 2006] With hybrid organic-inorganic solar cells, the titania can act as both an electron transport material and a phase separating material to limit the size of the photoactive organic layer to within the exciton diffusion length. By creating a heterojunction solar cell architecture with feature size below the exciton diffusion length, recombination loses can be minimized, leading to higher collection efficiencies. [Williams et al., 2008]

Titania nanostubes therefore offer not only great promise for generating better, inexpensive solar cell devices, but also have potential in a wide variety of other applications, as mentioned above. It is an interesting material system of practical importance.

1.1 Titania Nanostructures Synthesis Techniques

Material properties are linked to crystal structure and morphology, which are consequently dependent on the synthesis and processing conditions used to obtain the material. To understand how material structure, morphologies, and properties can be manipulated during the processing steps, an appreciation for the formation and synthesis techniques of titania nanostructures is needed.

Titania nanostructures can be synthesized in a variety of ways. The most common methods include sol-gel [Zhang et al., 2001; Traversa et al., 2000], vapor-solid-liquid (VLS) growth [Lee et al., 2006a], template assisted growth [Miao et al., 2002], hydrothermal [Kavan et al., 2004; Yuan and Su, 2004] and electrochemical synthesis [Zwilling et al., 1999; Gong et al., 2001; Macak et al., 2005a; Mor et al., 2003].

Sol-gel synthesis involves the use of suspended colloidal particles prepared from solution. Templates such as anodized alumina oxide (AAO) or polymer membranes can be immersed into the colloidal suspension, and the particles will fill the pores/channels of the template taking on their shape. After treatment to remove the template and the gel, the metal-oxide nanowire or nanotube is left. With this synthesis technique, the size and dimension of the resulting structure is dependent on the template into which the particles deposit, the composition of the sol-gel solution, and other processing conditions like deposition temperature and time. This method has been used to generate titania nanowire, nanotube, and nanorod structures. [Zhang et al., 2001] The nanostructures that are obtained however can often be bundled [Lakshmi et al., 1997], which limit their usefulness. In addition, the after-synthesis processing required to remove the template and isolate the nanowires formed can affect the structure and morphology of the resulting material.

In addition to its application in sol-gel synthesis, template assisted growth can also be performed with electrochemical deposition. Here, an oxide can be directly electrodeposited into a template (typically AAO) or metal can first be electrodeposited, and then heat-treated afterwards to form an oxide. Both the electrolyte in which the electrodeposition is performed and the template will affect the resulting oxide structure and morphology. Complications can arise from non-uniform deposition of material. This technique also encounters the same challenges as sol-gel in that the template needs to be removed after synthesis to obtain the nanostructured oxide. Nanowires synthesized with this method tend not to be organized and can clump together once the template has been removed. [*Miao et al.*, 2002]

Vapor-liquid-solid (VLS) growth is a popular growth method for generating uniform nanowires. The process starts with the dissolution of a gaseous reactant into a catalyst metal, present in liquid form. The catalyst provides an energetically favorable site for the absorption of the gaseous reactants, which then condenses within the catalyst, forming the basis for nucleation and growth of a single-crystalline material. For titania, a thermally evaporated Ti source can be used as the gaseous reactant and Au particles typically serve as the catalyst. [Lee et al., 2006a] The diameter of the resulting nanowire is dictated by the size of the Au catalyst, and growth of the material can be controlled via the growth temperature and pressure, as well as the choice of substrate material and templating the catalyst. While VLS growth can offer a high degree of control over the growth process, it is a complex synthesis method and requires not only a vacuum environment but also high growth temperatures due to the high melting point of oxides, or high vaporization temperature of the source metal.

Hydrothermal processes can also be used to produce nanostructured titania. The process uses an aqueous soluble metal-salt mixture, which acts as the precursor material required for synthesis. Upon heating the aqueous mixture at high temperature (between 100° C and 300° C) in a pressurized environment, metal-oxide nanostructures begin to form in solution. In the case of titania, synthesis typically requires autoclaving a mixture of TiO₂ powder dissolved in an alkaline solution. Ideally, the morphologies of the synthesized nanomaterials can be controlled by the processing parameters, including the structure of the starting precursor material, the nature and concentration of alkaline solution, and the reaction temperature and time. However, with the hydrothermal process, it is difficult to obtain materials with consistent and uniform structure and morphologies. In one growth session, synthesis can result in the formation nanotubes, rolled up sheets and flat sheet structure. [Yuan and Su, 2004] In addition, the process requires a high temperature and high pressure system, and is time consuming.

Of the fabrication techniques discussed, electrochemical synthesis yields the most uniform, highly organized, and oriented nanotube structures, which would be desirable for solar cell applications mentioned. In addition, the nanotubes, as formed, are mechanically and electrically attached to a conducting substrate, which could act as the current collector for many applications. The synthesis method involves immersing a metal substrate in an appropriate electrolyte and anodizing at constant voltage for a set period of time. Advantages of electrochemical synthesis include the fact that it provides a high degree of control over synthesis parameters (pH, electrolyte chemistry, substrate surface conditions, anodization voltage and time), which translates to control of synthesized material. Electrochemical synthesis is also easy and inexpensive compared to methods that require a vacuum environment, and can be performed at room temperature. In addition, a number of research reports have indicated that the particular nanotube architecture obtained via electrochemical synthesis gives titania nanotubes unique properties not seen in other forms of the oxide, making it of great scientific interest. [*Paulose et al.*, 2006; *Mor et al.*, 2005; *Zhu et al.*, 2007; *Shankar et al.*, 2008]

1.2 Electrochemical Synthesis of Titania Nano-tubes

1.2.1 Development of Methods

The development of electrochemically grown titania nanotubes has often been traced back to the investigations performed by Zwilling et al. [1999]. In this work, Zwilling and coworkers looked at the morphology, structure, and physicochemical properties of anodic oxide films grown on titanium and a TA6V (Ti-6% Al-4% V) alloy in a series of acidic electrolytes including chromic acid and hydrofluoric acid. They discovered that when Ti was anodized in fluorinated electrolytes, the oxide films that formed on the surface were nanoporous in nature, with a small amount of fluoride incorporated into the films. This discovery initiated a plethora of research on the subject of titania anodization and the electrochemical synthesis of nanostructured valve metal oxides. Gong et al. [2001] improved on the anodization methods and generated arrays of titania nanotube structures using an acidic electrolyte containing F^- anions. Macak et al. [2005a] further extended nanotube growth to neutral electrolytic solutions, which allow for the synthesis of longer nanotubes. [Paulose et al., 2006] Thus far, nanotube synthesis has been reported in many different electrolyte systems: with aqueous and organic solvents, acidic and neutral solutions, most of which contain fluoride ions as a principle component. [de Taconni et al., 2006; Macak et al., 2006; Feng et al., 2007; Yin et al., 2007 The move to organic solvents allows for the formation of smoother wall nanotubes as the increased viscosity of the solution slows down the growth process, and ensures a constant growth rate. [de Taconni et al., 2006]

While it has been suggested by various groups that the presence of F^- is essential to the formation of nanotubes [Zwilling et al., 1999; Yasuda et al., 2007; Raja et al., 2005], titania nanotube synthesis has also been achieved with non-fluoride containing electrolytes. Hahn et al. [2007] reported TiO₂ nanotube growth in HClO₄ and NaCl solutions, with 40V or higher anodization potential. Allam and Grimes [2007] also published work documenting nanotube growth using HCl electrolyte, but the synthesis conditions were very restrictive. Nanotubes could only be obtained in electrolytes with 3M or higher HCl concentration and a narrow anodization voltage range between 10V and 13V. The discrepancies in the literature indicate that there is uncertainty over the formation mechanism of titania nanotubes, and how the wide range of synthesis parameters affect nanotube growth.

1.2.2 Nanotube Morphology and Formation

The titania nanotubes that result from electrochemical synthesis have unique characteristics. First, the nanotubes are ordered structures, with similar tube diameter and length throughout the sample. (Figure 1.1) The diameters range from 10nm to 100nm, depending on synthesis conditions. The nanotubes appear uniformly across the surface of the Ti substrate on which they're grown in a close-packed manner. A sculpted barrier oxide layer exists between the nanotubes and the metal foil. What makes this a nanotube structure as opposed to a nanoporous structure are the distinct inner and outer tube walls that exist and the small separation between individual tubes. In addition, the tube's morphology consists of an open top and closed, rounded bottom, resembling a test tube structure. Lastly, the nanotubes are connected via a network of "oxide filaments" that run parallel to the Ti substrate surface and link adjacent nanotubes to one another.



Figure 1.1. SEM images of the (a) topview and (b) sideview of the nanotubes grown at 20V anodization in 0.15 M NH_4F .

The formation mechanism of anodic oxide films such as those found on titanium, aluminum, and tantalum have been the subject of extensive research. It is generally understood that the ionic current induced during anodic polarization of a metal leads to film formation. [Aladjem, 1973] The first step in anodic oxidation of titanium involves oxygen or oxygenated species absorbing on the surface of the air-formed oxide that covers the metal's surface. The anodic film then grows as a result of oxidation of Ti atoms, and field directed transport of the Ti⁴⁺ cations and O²⁻ anions through the film. Both Ti⁴⁺ and O²⁻ transfer contribute to film growth, although evidence suggests that growth takes place primarily at the oxide-solution interface. [Hall and Hackerman, 1953; Cover and Musselin, 1968] While this explains the formation of a compact oxide film during anodization, the actual mechanisms responsible for creating the unique titania nanotube morphology described above are under much discussion.

Although multiple models have been crafted to to explain the formation of nanotubes, they all agree on some general principles. [Yasuda et al., 2007; Raja et al., 2005; Taveira et al., 2005] Briefly, the first step in the formation process involves electrochemical oxide formation via the mechanism described above. This process can be expressed in terms of the following chemical reaction in the case of titanium:

$$Ti + 2H_2O \to TiO_2 + 4H^+ + 4e^-$$
 (1.1)

Next, an initiation step occurs to induce holes or pits in the oxide and these holes grow as the oxide thickens, creating channels that serves as the inner walls of the pores/tubes. The phenomenon responsible for growth of the holes has been attributed to chemical and/or field assisted dissolution. [*Prakasam et al.*, 2007; *Yasuda et al.*, 2007] Chemical dissolution is attributed to F^- ions in the solution, which participate in chemical etching:

$$TiO_2 + 4H^+ + 6F^- \rightarrow [TiF_6]^{2-} + 2H_2O$$
 (1.2)

Field assisted ejection of Ti⁴⁺ ions from the oxide to the electrolyte also plays a role in dissolution. Therefore, as the oxide thickens with anodization time, chemical and/or field assisted dissolution of the growing oxide is also occurring, essentially "drilling" holes in the oxide layer as the oxide/metal interface moves into the metal. Contrary to growth, a clear picture has not emerged on the initiation mechanism responsible for the ordered, homogeneous distribution of nanotubes that results from anodization. It has been proposed that random breakdown/pitting of the oxide [Taveira et al., 2005] or mechanical stress at the oxide/metal interface [Raja et al., 2005] is responsible for initiation, but neither of these mechanisms provides an adequate explanation of the process. The pitting mechanism is unlikely due to the fact that pitting is a very localized process and non-uniform process, and would not produce the observed homogeneous distributions of pores seen. Once a pit forms under freely corroding conditions or during galvanstatic polarization (the latter is the technique most often employed for growing anodized oxides), the pit grows while the area surrounding it is protected from pitting. [Fontana and Greene, 1967] The stress-based mechanism on the other hand postulates that stress at the metal/oxide interface, due to volume expansion of the oxide and electrostriction forces, induces a sinusoidal breakdown of the interface. The valleys of the sine wave are regions of high stress, which then preferentially attract the F^- ions that participate in oxide dissolution. For the stress mechanism to be an accurate description of the process, the assumption that F^{-} ions preferentially adsorb onto regions of high stress has to be true. However, this has no supporting experimental evidence.

Because titania is a highly functional material, a comprehensive appreciation of the atomic structure and growth dynamics of the nanotubes will enable materials engineering and optimization for specific device applications. The focus of this work is to examine the effects of synthesis conditions on nanotube formation and morphology in detail. The crystal structure and oxide composition that result from electrochemical synthesis will also be analyzed. Experimental results from both the synthesis and characterization work will shed insights into the growth and formation process of the nanotubes. As such, a more detailed discussion about the nucleation and growth mechanisms of titania nanotubes will be included later in the dissertation, after presentation of the experimental data.

Chapter 2

Experimental Methods

2.1 Electrochemical Synthesis: Experimental Set up



Figure 2.1. The experimental set-up used in electrochemical synthesis.

The electrochemical set-up used in this study for titania nanotubes synthesis is composed of a two-electrode cell, connected to a DC power supply. (Figure 2.1) Titanium foils (0.1mm, 99.6 purity, from Goodfellow) served as the working electrode while a platinum (Pt) mesh was used as the counter electrode. Prior to anodization, the Ti foils were sonicated in acetone and deionized water to remove oil, dirt and other debris, and then dried with flowing nitrogen gas. During the synthesis, the sample was immersed in the electrolyte while a constant cell potential between 6V and 40V was applied with the DC power supply for a period of 5 seconds to 15 hours. The solutions considered in this work varied in electrolyte composition and solvent identify. The solvents investigated ranged from deionized water, to the more viscous ethylene glycol and glycerol, to water-ethylene glycol and water-glycerol mixtures. Anions used in the electrolyte mixture included chloride, bromide, fluoride and sulfates, varying from 0.15M to 0.3M in concentration. All electrolyte solutions were prepared with reagent grade chemicals, and were mixed with a magnetic stirrer to ensure complete homogenization of solution before the anodization step. All nanotubes samples were synthesized at room temperature.

2.2 Characterization: Structure and Composition

A series of experiments were performed to examine the morphology, crystal structure, and composition of the nanotubes, as well as probe their properties. An FEI Strata 235 dual-beam scanning electron microscope was used to examine the morphology of the tubes. Side views and bottom views of the nanotubes were obtained by imaging sections of the sample that had been detached with a razor blade; no additional sample preparation was required.

Bright field transmission electron microscopy (TEM) was carried out on the 200kV Phillips CM200 FEG microscope and the JEOL 200CX, while high-resolution TEM was performed using the FEI monochromated F20 UT Tecnai. Selected area diffraction (SAD) and digital diffractograms of the nanotubes were also obtained on these instruments. Information about oxide composition was acquired via energy dispersive X-ray spectroscopy (EDS) analysis performed on the CM200. Spot scans and line scans were performed, employing a 1 nm beam size. Electron energy loss spectroscopy (EELS) analysis was performed on the Tecnai, utilizing the instrument's elemental mapping capabilities.

2.2.1 ImageJ Particle Analysis

A series of SEM images were processed and analyzed using ImageJ, an open source image processing program developed by the National Institute of Health, to determine the tube/pore count and diameter size under various growth conditions. The images were altered to an 8-bit image and the black/white threshold values set so that the inside of each tube/pore is black, while the space in between tubes is white. ImageJ automated particle analysis tool was then utilized to count the pores, with each pore being considered a particle. The program outputs the total "particle" count, as well as the average size of the particles (in terms of pixels²) and their average diameter (pixels). By measuring the pixel length of the scale bar in each image, the pixel dimensions can be converted to real dimensions via a pixel/nm conversion factor.



Figure 2.2. Example of an SEM image before (a) and after processing (b) in ImageJ and the results output by the "particle analysis" tool.

2.2.2 TEM Sample Preparation

Thin, electron transparent, cross-sectional samples were required for TEM, EDS and EELS analysis. Sample preparation involved gluing two anodized samples together using a high temperature epoxy (G1 Bond) before subsequent cutting, polishing, and ion milling steps. Thick silicon pieces are also glued on the outer edges of the foil samples, creating a sandwich structure, so that a 3mm circular disc cross-section could be obtained. The thin (approximately 500 microns), circular disks are further thinned using the D500i Dimpler (by VCR Incorporated) and ion milling. A number of ion mills were used including the Gatan Precision Ion Polishing System (PIPS), the Technoorg LINDA IV3H/L, and Fischione Instruments Model 1010 Ion Mill. The end product is a sample that is approximately 10-15nm thick through its thinnest area, making it electron transparent. The sample is then carbon coated to eliminate charging in the microscope. (Figure 2.3)



Figure 2.3. The steps involved in generating a cross-sectional sample for TEM analysis.

Chapter 3

Influence of Processing Parameters on Nanotube Growth and Morphology

Electrochemical processes offer precise control of critical synthesis parameters, allowing for the production of specific, desired morphologies or structures. In order to take advantage of this capability, an understanding must be established as to how the synthesis conditions affect the formation of the structures. This chapter examines some growth parameters and their effects on titania nanotube growth and morphology.

3.1 Anodization Voltage and Time

Among the key parameters that can be controlled during electrochemical synthesis are the anodization potential and anodization time. The anodization potential sets the driving force for metal oxidation and oxide growth, while the anodization time provides an uninterrupted period during which the process can occur. Most anodized oxide films form according to the high field model, which requires ion migration and diffusion for film growth. The transport of ions through the oxide is explained via field directed, thermally activated hopping. At low field strengths (E <10⁵ V/cm), the model results in ohmic behavior, while high field strengths (E >10⁶ V/cm) lead to a current density that is exponentially dependent on the field strength:

$$i = i_o \exp(\beta E_s) \tag{3.1}$$

where β is an activation energy constant between 0 and 1, and E_s is the field strength. [Schultze and Lohrengen, 2000] Additionally, according to Faraday's law, the resulting oxide thickness d is related to charge q:

$$d = \frac{qM}{zr\rho F} \tag{3.2}$$

M is the molecular weight of the oxide, r is its roughness factor, and ρ is the density, assuming a homogeneous oxide. By combining equations (3.2) and (3.1), we get an expression for the growth rate:

$$\frac{dd}{dt} = \frac{Mi_o}{zr\rho F} \exp(\beta E_s) \tag{3.3}$$

where z is the number of electrons and F is Faraday's constant.

Equation (3.3) suggests that while the growth rate slows with time, the thickness of the oxide layer continues to increase with prolonged anodization time. However, with metal anodization processes that result in a planar passive oxide, the final oxide thickness is limited by the anodization voltage, rather than anodization time. This is because while oxide growth is occurring, dissolution is also taking place at the oxide/electrolyte interface. Therefore, steady state is reached when the growth rate is equaled to the dissolution rate of the oxide. According to the high field model, the relationship between applied voltage and planar oxide thickness of anodic films grown on Ti and its alloys is approximately 2 nm/V [*Aladjem*, 1973], without much scatter in the data points. The range of experimentally measured thickness is reported to vary between 1.8 nm/V [*Green and Sedricks*, 1971] to 2.4 nm/V [*Cover and Musselin*, 1968].

If the given thickness/voltage relationship above holds true for nanotube synthesis, then a 20V anodization voltage should yield a titania nanotube array that is limited to 40nm in length. However, nanotubes grown at 20V can actually reached microns in length. Contrary to what is seen in compact oxide growth, time is the limiting parameter when it comes to length of the nanotube oxide layer. The longer the metal foil is anodized, the longer the nanotubes that form on the surface. The relationship between growth time and tube length is not linear however, with most of the tube growth occurring in the first 30 minutes of anodization, achieving approximately 1 micron in length. The growth rate then drops off, where even after 15 hours of anodization, the nanotubes are only 3 microns long. (Figure 3.1) The relationship described in Figure 3.1 holds true for Ti foils anodized at one potential (20V in this case) in ethylene glycol containing $0.15M \text{ NH}_4F$. Because the electrolyte chemistry (tied to solution conductivity and ion mobility) and anodization potential (reaction driving force) affect current flow in an electrochemical system, changing these parameters will also change the growth rate. Prakasam et al. [2007], who also examined nanotube formation in ethylene glycol (EG) based electrolytes, reported that both the concentration of F^{-} in solution and the percent volume of water (varying from 1-3%) mixed in with EG affect the length of the nanotubes. Additionally, they found that with a 17 hour anodization time in EG electrolyte containing 0.3 wt% NH₄F and 2 vol% H_2O , the higher the anodizing voltage (20-65 V), the longer the resulting nanotube length (5-105 microns).

In the case of nanotube growth, the anodization voltage does not affect the thickness of the nanotube layer but rather the dimensions of the tubes, specifically their diameter. Figure 3.2 presents four different Ti foil samples that were anodized at various potentials for 1 hour. The type of substrate, pre-anodization sample prep, and experimental parameters (except



Figure 3.1. Anodization time vs. nanotube length for titania nanotubes synthesized in ethylene glycol with 0.15 M NH_4F .

for voltage) were the same for all the samples. For the sample formed at 10 V anodization, the resulting oxide is porous instead of tubular in structure, and the diameters are quite small, around 21 nm. With 20 V anodization, the diameter increase to 40nm and a clear tubular structure emerges, with an inner and outer tube wall. At 30 V and 40 V, the tube structure is maintained and the average diameter increases. It is observed that nanotubes grown at one anodization voltage have very similar diameter values, with small deviations from their average. The diameter and voltage relationship is approximately linear (Figure 3.3) in nature. The results from these synthesis runs indicate that 1) in a given electrolyte system, the higher the anodization potential the larger the tube/pore diameter, and 2) there is an optimum diameter value per given anodization voltage. The relationship between anodization voltage and diameter suggests that the nanotube diameter at a specified applied voltage is an optimum value that balances energetic contributions from the applied field, surface energy, and other driving forces. As such, nanotubes with diameters smaller than the optimum value grow, while those with diameters larger than the optimum value split (Figure 3.4) in order to achieve the equilibrium state.

When examined in detailed, the results seen in this study are not inconsistent with the high field model of oxide growth. In planar oxide growth, the electric field strength in the oxide decreases as the oxide thickness increases, thereby reducing the ability of ions to migrate and participate in growth. As a result, the final oxide thickness is limited by the applied voltage. For the nanotubes, because of their morphology, the electric field strength through the oxide does not decrease with increasing nanotube length, as the thickness of the tube bottom remains the same throughout most of the growth stage. Figure 3.5 presents a schematic



Figure 3.2. Nanotubes anodized in 0.15M NH₄F in EG at 10V, 20V, 30V and 40V.

diagram of the nanotube and metal substrate on which the tubes form. As the oxide/metal interface moves into the metal with oxide growth, so does the electrolyte/oxide interface at the tube bottom, maintaining a consistent oxide thickness. This allows the nanotubes to elongate with increased anodization time. Another factor to consider is the dissolution of the oxide. Because anodization is occurring in an electrolyte that is simultaneously chemically etching the oxide (Equation 1.2), dissolution is occurring throughout the nanotube. For the tube length to elongate with anodization time, this means that the oxide dissolution rate is nonuniform, with the oxide at the tube bottom dissolving at faster rate than oxide at the tube top. Recalling Equation 1.1, we see that oxidation of metal generates excess H⁺ ions at the tube bottom. This generates a pH gradient through the length of the tube and results in non-uniform oxide dissolution. [Macak et al., 2005a] Bright and Readey [1987] have shown that the dissolution kinetics of TiO₂ is affected by solution pH, with increased dissolution rates seen in lower pH electrolytes. In addition, due to the direction of the applied field in the oxide during growth, Ti⁴⁺ ions are also being ejected into the electrolyte near the oxide/electrolyte interface. This field-assisted dissolution contributes to the fast dissolution rate near the tube bottom, where the field strength is the highest.



Figure 3.3. The voltage vs. diameter relationship of titania nanotubes synthesized in 0.15 M NH₄F in ethylene glycol.



Figure 3.4. The arrow points to a nanotube that had grown too large in diameter and had to split into two in order to maintain the optimum diameter value dictated by the anodization voltage.

While the tube length is not limited by the anodization potential, the experimental results do indicate that the growth rate decreases with time. If the oxide thickness on the bottom of the tubes does not change with time (for most of the growth stage), then the tube bottom is at some limiting thickness. Therefore, for the tubes to elongate, dissolution must occur



Figure 3.5. Schematic diagram of nanotube cross-section.

at the oxide/electrolyte interface in order to enable further oxide growth at the oxide/metal interface. Thus, the oxidation rate (i.e. growth rate) is limited by the oxide dissolution rate at the bottom of the tube. The nanotube structure allows electrolyte to fill the inside of the tubes, providing the ionic species required for oxide dissolution and further oxide growth to the tube bottom. However, the longer the tubes, the longer the transport path for ionic species, which travel via diffusion in the electrolyte. Crevices are characterized by diffusion limitations and so the electrolyte inside them is likely to be different from that seen in the bulk solution. [West, 1980] If regions inside the nanotubes are treated as small crevices, where the electrolyte is allowed to develop a composition different from the bulk then the dissolution rate and growth rate are likely related to the transport of ionic species inside the tube. As described above, for the tubes to grow, the rate of dissolution at the tube opening must be slower than the dissolution rate at the tube bottom. Therefore, when the nanotubes get long enough so that transport of species from the bulk solution to the tube bottom limits the dissolution rate at the bottom, and it approaches the dissolution rate at the tube top, then the growth rate decreases. Simply, when the dissolution rates at the two ends of the nanotubes get closer to one another, the growth rate will decrease, and when the dissolution rates are equal, the growth rate will be zero.

3.1.1 Evolution of the Nanotube Structure

To study how the nanotube structure evolves with time, an experiment was performed to look at the different stages of nanotube formation. This involved stopping the synthesis at various steps during the early part of the growth process. Figure 3.6 shows 5 different samples, anodized for 30 seconds, 60 seconds, 5 minutes (300 seconds), 15 minutes, and 1 hour in EG containing 0.15M NH₄F. In less than 30 seconds of anodization, a porous oxide layer appears on the surface of the sample. These pores are extremely small (nm in size) but they are fairly uniform over the entire surface of the sample. The porous layer evolved with time, yielding larger pores with longer anodization time. Images from after 15 minutes of



Figure 3.6. Anodization time vs. nanotube length for titania nanotubes synthesized in 0.15 M NH₄F in ethylene glycol.

anodization show that while the porous layer was still present on top, nanotubes had begun to develop underneath the porous layer. The sideview insert in the micrograph in the upper right hand corner of Figure 3.6 shows the tubular structure. These tubes, about 400nm in length, appear not as uniform as tubes that were formed after one hour of anodization (Figure 3.6). The experiment reveals that growth of titania nanotubes is a multistep process, involving the initial formation of a porous top layer, which later dissolves entirely, leaving the nanotubular oxide on the surface of the substrate. In addition, the results suggest that there is a minimum growth time required for the formation of organized, uniform nanotubes.

3.2 Effect of Electrolyte Chemistry: Anions and Solvent

A series of studies were performed to investigate how different anion constituents in the electrolyte affect nanotube formation and growth. Titanium foils were anodized in electrolytes containing 0.15 M NH₄F, 0.15 M-0.3 M NaCl, 0.15 M-0.3 M KBr, and 0.15-0.3 M NH₄(SO₄)₂. Chloride and bromide were chosen for the study because they, like fluoride, are halides, and might have a similar effect on Ti anodization. The various solvents examined were deionized water, ethylene glycol (EG), glycerol and mixtures of EG-water, and glycerol-water. The applied voltage during anodization ranged from 20 V to 40 V.

As described in Chapter 2, anodization of Ti in a F^- containing electrolyte results in an oxide with unique morphology. Mainly, oxide nanotubes are formed with ordered, closepacked structure. The tubes have similar diameters, approximately 40 nm for an anodization potential of 20 V, and are essentially the same length across the surface of the Ti substrate.

Anodization of titanium in sulfate containing electrolytes, regardless of applied cell voltage (10 V - 40 V), resulted in a compact oxide layer. (Figure 3.7). In both cases of NaCl and KBr based electrolytes, tubular structures were formed at both applied potentials of 20 V and 40 V. These tubes, however, have some differences in morphology from those formed in F^- based electrolytes. For one, the tubes appear only in selected areas, where pitting of the metal has occurred, as opposed to uniformly over the entire surface of the substrate. The tubes also have typical diameters of approximately 15 nm, which is significantly smaller than the 40 nm to 100 nm diameter tubes formed in F^- solutions at the same applied potential. The diameter of the tubes appeared to be independent of anodization voltage.

The identity of the solvent used for synthesis also affected the growth rate and morphology of the nanotubes. Anodization performed in viscous non-aqueous solutions (EG or glycerol) with Cl⁻ and Br⁻ ions yielded nanotubes that are very short in length. As shown in Figure 3.8, the tubes (structures with inner and outer tube wall) only appeared in pits that had formed in the titanium foil via attacks by Br⁻ and Cl⁻ ions. The tube diameters are the same as those formed in the aqueous Cl^- and Br^- electrolytes, about 15 nm, but are limited in length to a few nanometers. Different anodization times of 30 and 60 minutes yielded the same length of nanotubes. In aqueous electrolytes, no pits were obvious after anodization. Instead, as shown in Figure 3.9, the surface of the metal was covered with a compact oxide layer, with clusters of overgrown nanotubes or nanofibers. It is difficult to determine with certainty whether tubes or fibers, as presented in Figure 3.9c, had formed in this case. Top view images of the bundles could not confirm the existence of a tubular structure, and thus these will be referred to as fibers. The fibrous structures appeared in clusters, lying on top of the anodized surface (Figure 3.9). It is suspected that pitting of the titanium initially occurred in these areas, and the fibers grew from the pits. With only 60 seconds of anodization time, the fibers grew up to tens of microns in length. On the contrary, tubes grown in F^- based electrolytes have a much slower growth rate (initial rate of 1 micron in 30 minutes). The fibers, grown in aqueous chloride, have the same diameters as the tubes grown in the viscous electrolytes.

In electrolytes with mixed water-ethylene glycol or water-glycerol compositions (50/50 volume mixture), very long, more ordered, and well-defined tubes were formed. Again, the tube structure appeared in clusters, often resembling a flower with petals composed of bundled tubes, radiating from the center (Figure 3.10a). Many differences exists between the nanostructures formed in the mixed solvent electrolyte and the structures formed in aqueous electrolytes. In the aqueous electrolyte, more pitting/cluster sites formed on the



Figure 3.7. Compact oxide formed after anodization of Ti in EG with $0.3 \text{ M NH}_4(SO_4)_2$.



Figure 3.8. (a) Nanotubes formed inside a pit. This sample was anodized at 20V for 30 min in ethylene glycol containing 0.15M KBr. (b) Nanotube layer found near the edge of a sample anodized at 20V for 30 min in ethylene glycol containing 0.3M NaCl.

oxide surface (Figure 3.9a). Even though there are fewer cluster sites in the mixed waterethylene glycol or water-glycerol case, the clusters are larger, and have longer tubes (Figure 3.10a). More importantly, the tube structure is very apparent in the mixed solvent case, with the tube opening clearly visible ((Figure 3.10) c and d).

The concentration of Cl⁻ and Br⁻ ions in solution affected the number of nanotube-



Figure 3.9. (a, b) Nanofiber clusters lying on top of the compact oxide layer. These fibers were formed on Ti foils anodized at 40 V for 60 s in 0.3 M NaCl. (c) Magnified view and (d) top view of the fibers.

cluster sites on the oxide surface. Higher molarity electrolytes resulted in a larger number of clusters. Similarly, higher anodization voltages also lead to more cluster formation. The voltage however did not have an effect on the diameter of the tubes, which is contrary to the case in F^- based solutions, where higher voltages give larger tube diameter. Here, anodization voltages of 20 V and 40 V produced the same size tubes. The edges of the sample, where the current densities are high, had the highest number of clusters, and consequently nanotubes. In areas near the edge, an organized layer of tubes could be seen (Figure 3.8b). Prolonged anodization of the sample, however does not lead to the spread of the organized layer of tubes but instead causes dissolution of the Ti foil.



Figure 3.10. Nantubes synthesized in a 50/50 water-ethylene glycol mixture containing 0.3 M NaCl or 0.3 M KBr. The samples were anodized at 40 V for 60 seconds. (a) Nanotube clusters on the compact oxide layer. (b, c) Side view and top view of nanotubes formed in 0.3 M NaCl. (d) Side view and top view of nanotubes formed in 0.3 M KBr.

Several different factors from this experiment suggest that the growth mechanisms of nanotubes formed in Cl^- and Br^- electrolytes are different from those of tubes synthesized in F^- solutions. First, the anodization voltage did not dictate the diameter of the tubes, as seen in F^- based growth. Regardless of the anodization voltage, the nanotubes' diameter was limited to 15nm. In addition, the tubes examined in this study have a much faster growth rate, and their morphology is different than F^- grown tubes. Tubes grown in Cl^- and Br^- electrolytes tend to appear in patches and form bundles, with very high aspect

ratio nanotubes, while F⁻ based tubes grow more slowly and cover the surface of the Ti in a homogeneous manner.

To examine the growth of these nanotubes in more detail, a cross-sectional sample was prepared using a focused ion beam (FIB) to locally remove materials. Before the crosssection was cut out with the FIB, a top layer of platinum was deposited to preserve the nanotube clusters during the process. Figure 3.11 shows both the top-view with the Pt layer (a) and the cross-sectional view of the nanotube cluster (b), and confirms that tube bundles were formed over regions of pitted oxide/metal. Figure 3.11b and Figure 3.12 clearly show the large region of oxide that had grown into the metal foil, and the porous nature of this oxide. Clear "cracks" are visible in the side view, which shows area where the oxide had split, providing a path for the electrolyte to penetrate and further pit the sample. The crosssectional image supports the pitting hypothesis for chloride and bromide nanotube-cluster growth, as most pits that form tend to undermine the surface as they grow and are very localized. [Fontana and Greene, 1967] Another observation that supports a pitting-related mechanism of nanotube formation is the presence of patches or clusters of nanotubes that appear adjacent to regions of unaffected planar oxide. This behavior is indicative of pit formation, where a pit forms in anodic areas, and by growing, it protects the regions around it from pitting. In the case of nanotube formation, the applied current is focused to the already formed pits so that the regions outside the pits are not strongly polarized anodically. Consequently, pits are less likely to nucleate at sites in the vicinity of a pit, as seen in the images.



Figure 3.11. (a) Topview of nanotube clusters, showing Pt deposition layer on top and (b)Cross-section view of the nanotube cluster grown in $50/50 \text{ EG/H}_2\text{O}$ containing 0.3 M NaCl.

The growth mechanism in this case likely involves initial dissolution of the surface oxide and pitting of the metal via Cl^- and Br^- anions at random locations on the surface of the oxide. The pitting then generates local regions of low pH which further enables oxide



Figure 3.12. Magnified view of the nanotube cluster cross-section shown in Figure 3.11.

dissolution, where smaller pits form. The dissolved Ti^{4+} flow from the pit towards the bulk electrolyte due to the concentration gradient that develops and deposits on the outer edges of the pit, where they combine with oxygen ions from hydroxide species in solution, forming tubular oxide structures. The hydroxide and oxygen concentration also vary along the length of the tube, leading to preferential deposits of oxide near the tube opening. Tube growth therefore should occur at the top, which is in accordance with experimental results. The overflowing nature of the nanotube clusters on the top oxide suggests a mechanism where nanotubes grow out of the pits that had formed. This is similar to a mechanism proposed by *Riggs et al.* [1960] to explain the formation of tubular corrosion products that formed on steel. While studying the effect of pH on oxygen corrosion of steel, Riggs and co-workers discovered that steel samples immersed in a 5% NaCl brine solution at pH 12 showed extremely severe localized corrosion that produced what the authors reported as filament or whisker growth.
However, they also observed that these whiskers were actually hollow tubes, with diameters that span from 10 microns to 4 millimeters. The formation of these tubular corrosion product was attributed to deposits of ferrous hydroxide on the edges of an anodic pit. The ferrous hydroxide forms by corrosion products in the pit combining with hydroxide species in the electrolyte, and is rapidly oxidized to various iron oxides by dissolved oxygen in the solution.

Pitting of metal is associated with halide ions, with chloride and bromide being the most aggressive pitting agents. Fluoride and iodide ions on the other hand have shown relatively little pitting tendencies. [Fontana and Greene, 1967] As seen by the experimental results, nanotubes formed in Cl^- and Br^- containing electrolytes appear in regions of pitted metal, while those formed in F^- containing electrolyte appear uniformly over the surface of the metal substrate. Therefore, while pitting adequately explains the formation of tubular structures formed in chloride and bromide containing solutions, it does not appear to provide a satisfactory mechanism for titania nanotubes formed in fluoride based solutions.

3.3 Surface Oxide Condition

As mentioned in Chapter 2, it has been suggested that the initiation of pores, which grow into organized nanotubes, is a result of random pitting processes [*Taveira et al.*, 2005] or mechanical stress at the oxide/metal interface [*Raja et al.*, 2005]. To investigate these claims further and study the effect of the surface oxide condition on nanotube formation, a series of time progression experiments was carried out. The first study involved the growth of nanotubes in a 2-step anodization process. In the first step, the Ti foil is anodized in a sulfate containing solution to form a compact oxide layer. Based on the model of high-field oxide growth, with an anodization voltage of 20V, the thickness of the compact layer should approximate 40 nm. [*Aladjem*, 1973] This is much thicker than the native oxide on Ti, which typically ranges from 1 to 7 nm [*Aladjem*, 1973; *Schultze and Lohrengen*, 2000]. Next, the sample with the compact oxide is then rinsed, dried and re-anodized in a 0.15 M NH₄F electrolyte to form nanotubes. Samples were taken at various time steps in the anodization process to examine the evolution of the oxide/electrolyte interface as nanotube formation takes place. Figure 3.13 shows the time progression that ensued during anodization in a fluoride based electrolyte.

The second experiment also involved a 2-step anodization process. In the first step, the Ti foil is anodized in a fluoride containing electrolyte for 1 hour to generate organized nanotubes. The tubes were then removed via sonication in a 1 part ethanol and 4 parts water mixture solution, leaving just the sculpted barrier oxide layer on top. This generates a metal foil with a dimpled oxide surface for the second anodization step, which was also in a F^- based electrolyte. This experiment tests the effect of "patterned substrate" surface on subsequent nanotube growth. Again, samples were taken at various points of the anodization process to examine the progression of nanotube formation. (Figure 3.14 and 3.15)

If the random breakdown/pitting mechanism is correct in describing the initiation of nanotubes, then with dimples/pre-formed pits on the surface of the foil acting as ready



Figure 3.13. Time progression of nanotube formation with an initial compact oxide present.

initiation sites, the pits/dimples should simply elongate and grow deeper into the oxide/metal interface forming pores. Similarly, if the valleys of the dimples are regions of high stress that preferentially attracts F^- , then the bottom of the dimples should continue to get etched as the oxide grows. This in fact, was not observed experimentally. Mainly, the dimples/pits did not act as initiation sites, and they did not extend deeper into the oxide with time. Instead, after 30 seconds of anodization, small pores appeared inside and under the dimples. Within each dimple, 2 or 3 pores had initiated after this short anodization time. As the 60 seconds and 5 minute images show, these newly initiated pores get larger with time. By 15 minutes, the outer dimpled-oxide layer has completely dissolved, leaving just the new porous layer on the surface. These pores increased in diameter with time, going from 24 nm at 15 minutes, to 33 nm after 1 hour of anodization. Table 3.1 summarizes the particle analysis performed in ImageJ to determine the pore count and average pore diameter after each time step examined. Data for the 30 second anodization step was not included because the image did not have enough contrast between the hills and valleys of the dimples to be processed in ImageJ. The pore count and diameter data suggests that as time progressed, the number of pores decreased and the average diameter increases. The only outlier in this trend is the 60 second sample, which has a smaller pore count and larger diameter than the 5 minute sample. Close examination of the 60 second sample, however, reveals that some of the newly initiated pores are very shallow, thus not offering the contrast required for their inclusion in the ImageJ particle analysis. The results suggests that the formation process



Figure 3.14. Time progression of nanotube formation with a dimpled surface oxide present.

involves nucleation of small pores that then coalesce into larger pores at some steady- state diameter size. While the resulting pores/tube structure was more organized, the formation process seems to involve the same steps as that seen in Figure 3.6. This experimental result suggests that growth of the nanotubes is controlled by "conditions" at the oxide/electrolyte interface beyond the mere shape of the interface. Conditions might mean the composition of the electrolyte adjacent to the oxide and/or the composition of the oxide adjacent to the electrolyte.

The second experiment, nanotube growth with an initial 40nm-thick compact oxide layer present, provides a similar result. Figure 3.13 reveals that after 30 seconds of anodization, the

Time (min)	Pore Count	Diameter (nm)
1	929	26.8
5	1089	24.2
15	915	24.4
30	897	28.8
60	811	33.2

Table 3.1. Summary Data of Pore Growth with a Dimpled Surface



Figure 3.15. A close-up view of the images presented in Figure 3.14.

compact oxide has obtained small pores throughout the surface in a non-uniform manner, in patches. The density and size of these pores increased with time (60 seconds and 5 minutes) and coalesced to form cracks or larger holes on the surface. However, while large regions of the surface oxide was dissolving, other regions of the oxide appeared immune to pore formation and remained compact. Looking through the larger holes and regions of dissolved surface oxide, we see that small pits had formed in the oxide growing underneath the surface oxide (starting from the 5 minute sample). These holes increased in diameter with time, and after 30 seconds of anodization, the top-view image showed that a clear nanotube morphology had developed. However most of the surface of the sample was still covered with the initial compact oxide, which was in the process of being dissolved. After one hour of anodization, most of the initial oxide had been removed, revealing the uniform nanotube layer that had formed underneath. ImageJ analysis was not performed in this case because of the non-uniformity of the surface.

The results from these experiments indicate that pore initiation/growth is a dynamic process involving oxide that is currently being formed via anodization in a fluoride containing solution. The pre-formed "pits" in the experiments merely provided a screening effect from the electrolyte but did not act as initiation sites. Smaller pores initiate inside the "pits" and these grow to form the final porous oxide that appears after 1 hour of anodization. In the experiment involving an initial compact oxide layer, the compact layer gets etched but not uniformly. Instead small holes appeared in the top oxide, providing a path for the electrolyte

to get to the actively forming oxide layer. The compact oxide simply acts as a "dead layer" that needs to be shed. The eventual dissolution of the top compact oxide reveals uniform nanotubes underneath. The mechanism of nanotube formation, regardless of the surface condition (native oxide, dimpled oxide, or thick compact oxide) appears to be the same. It involved the initiation of many small pores at the surface of the actively forming oxide, which grows and coalesce to form larger pores that result in nanotubes.

3.4 Multi-step Anodization Processes

To test the hypothesis that pore growth is a dynamic process which involves only "active oxide" currently being formed via anodization, a series of multi-step anodization experiments were performed. In the first experiment, sample Ti foils were anodized at 20V in a fluoride containing electrolyte for 1 hour. The samples were then taken out of solution, rinsed with deionized water, dried, and then re-immersed in the growth solution and anodized at the same potential for another hour. The result of the synthesis is presented in Figure 3.16.



Figure 3.16. Nanotubes grown via a 2-step anodization process. The sample was anodized at 20V for 1 hour, taken out of solution, rinsed, and dried before re-anodizing at 20V.

It has been established by the results presented in Figure 3.13 that a sculpted oxide

surface does not enable tube growth, without the "re-nucleation" of the pores/tubes. In this experiment, not only the sculpted interface but the entire tube morphology is maintained. The only variable in the experiment is the electrolyte chemistry inside the tubes, which is changed from what develops during active growth to the bulk electrolyte upon re-immersion of the sample. If the unique tube morphology is enough to maintain further elongation of the tubes with anodization time, then a second nucleation step should not be necessary. However, as shown in Figure 3.16, two layers of nanotubes are clearly present in the sample, indicating that upon re-anodization, nucleation occurred in the barrier layer oxide and produced new tubes that grew underneath the original nanotube layer. The new nanotubes appear to nucleate and grow in between existing nanotubes. This result is consistent with what is known about the tube growth process. During anodization, a pH gradient is maintained inside the tubes to induce non-uniform oxide dissolution along the tube's length, enabling further tube growth. [Macak et al., 2005a] When the anodization is stopped, and the solution inside the tubes is replaced with the bulk solution, the unique environment required for tube growth is no longer there and nucleation must occur in order to re-establish those conditions. Results from this experiment indicate that the electrolyte chemistry directly in contact with the growing oxide plays a key role in the formation of nanotubes.

To test the importance of the electrolyte chemistry further, a second experiment involving a 2-step anodization process was performed. Foil samples were first anodized at 20V in a fluoride containing electrolyte to form nanotubes. The anodization was then paused, by turning off the power supply, for 30 seconds to 5 minutes and then resumed at the same voltage for another hour. The samples and the solution were not disturbed during the pause. Figure 3.17 shows the samples that result from a) the 30-second pause and b) the 5-minute pause. When the anodization is paused for only 30 seconds, the nanotubes that were present continued to grow, creating one continuous nanotube layer on the Ti foil. In the sample where the anodization was paused for 5 minutes, two nanotube layers are clearly present, indicating that a second nucleation process had occurred.

The results once again highlight the importance of the chemistry near the oxide/electrolyte interface. It should be emphasized that the chemistry/composition of the oxide as well as chemistry of the electrolyte at the oxide/electrolyte interface might be important factors in the nucleation and growth of nanotubes. A short pause of 30 seconds is not long enough to change the electrolyte and oxide chemistries inside the tubes, and the nanotubes already present on the foil continue to grow with the second anodization step. No re-nucleation step is required for this process. However, if the pause is 5 minutes long, nucleation is then required to establish the electrolyte and oxide chemistries needed for growth. To understand the possible changes in chemistry in the oxide and electrolyte that could occur within a 5 minute timeframe, transport of species in the liquid electrolyte and solid oxide are examined.

Ionic species in solution travel via diffusion, and therefore, to understand their movement in the electrolyte Fick's laws of diffusion can be used. Fick's first law relates the flux to the concentration field, stating that species diffuse from regions of high concentration to regions



Figure 3.17. Two-step anodization synthesis with (a) a 30-second pause, and (b) a 5-minute pause halfway through the 2-hour synthesis run.

of low concentration. For a one dimensional case, this is:

$$J = -D\frac{\partial\phi}{\partial x} \tag{3.4}$$

where J represents the flux, D is the diffusion coefficient and ϕ is the concentration. Fick's second law indicates how the diffusion driven transport of species causes the concentration field to change with time:

$$\frac{\partial \phi}{\partial t} = -D \frac{\partial^2 \phi}{\partial x^2} \tag{3.5}$$

By combining Fick's first and second laws, an expression can be obtained to indicate how far a given specie has traveled in one dimension during a given period time, if the diffusion constant D is known. This is called the diffusion length:

$$x = 2\sqrt{Dt} \tag{3.6}$$

Most aqueous species have diffusion coefficients that differ, at most, by a factor of two from the self-diffusion coefficient of water, which ranges from 2.2 to $2.6 \times 10^{-5} \text{cm}^2/\text{sec}$ at 25° C. [Mills, 1973] Assuming that the diffusion constant of F⁻ and other ionic species in the electrolyte is similar to water, and using Equation (3.6) to solve for the time it would take the ions to travel down a 2 micron long channel, the resulting transport time is 0.0005 seconds. While this value is small, it does not take into account some other factors that could affect the diffusion coefficient, such as solution viscosity. From the Stoke-Einstein relationship, it is clear that electrolytes with higher viscosity values will yield lower diffusion coefficients D:

$$D = \frac{k_B T}{6\pi\eta a} \tag{3.7}$$

where k_B is Boltzmann's constant, T is temperature, η is the viscosity of the solution, and a is the radius of the spherical particle (ion in this case). If the viscosity of ethylene glycol (0.016 Pa·s) is substituted into the equation instead of the viscosity of water (0.0008 Pa·s), the transport time for ions to travel 2 microns down the length of the tube is 0.01 seconds.

In the experiment, the unique electrolyte and oxide chemistries within the nanotubes were still maintained 30 seconds after the anodization was stopped. The experimental time, 30 seconds, is three orders of magnitude slower than the expected transport time. To ensure that the effects seen are indeed associated with compositional changes in the electrolyte as opposed to changes in the oxide, the room-temperature transport rate of ions in solids were examined. Studies by *Maier et al.* [1976] about the self-diffusion of Ni at low temperatures gives information about the diffusivity of cation species. It is found that Ni self-diffusion occurs at a rate of $2.58 \times 10^{-18} cm^2/s$ at 542° C. At room temperature, this value is expected to be much lower, since the diffusion coefficient is dependent on temperature as described by an Arrhenius equation:

$$D = D_o e^{\frac{-Q_A}{RT}} \tag{3.8}$$

where D is the diffusion coefficient, D_o is the maximum coefficient at infinite temperature, Q_A is the activation energy, T is the temperature and R is the gas constant. However, assuming $D=2.58 \times 10^{-18} cm^2/s$, the transport time required for cations to travel 40nm (the thickness of the oxide) is still 1.5×10^6 seconds, which is five orders of magnitude slower than what was seen experimentally. With a slower, room-temperature diffusivity constant, the transport time will be even slower. This leads to the conclusion that changes in the electrolyte chemistry is most likely responsible for allowing nanotube growth or requiring nucleation.

Because of differences in the calculated and observed transport time, however, it seems inconceivable that diffusion alone is limiting the movement of ionic species inside the tube. Other factors could be influencing ionic mobility in the electrolyte. These include the solution inside the nanotubes being over-saturated with ions (Ti^{4+} , H^+ , etc...), which would affect their mobility. The presence of a retained electric field after the applied voltage has been turned off could also slow down the movement of charged species. What is clear from these experiments is that the maintenance of a unique electrolyte composition in the nanotubes, adjacent to the oxide/electrolyte interface, is critical to nanotube growth. On the other hand, the morphology of the interface (dimpled vs. planar), or the presence of pre-existing nanotubes, do not dictate growth conditions.

3.5 Nanotube Stability

Most applications that make use of nanostructured titania utilize the crystalline form of the oxide, anatase or rutile, depending on the specific application. [*Park et al.*, 2000; *Mor et al.*, 2005; *Adachi et al.*, 2000] This is due to the fact that the crystalline titania exhibit many of the electrical and optical properties desirable for device applications, while the amorphous oxide contains trap states and defects that make them non-ideal semiconductor materials. As titania grown via anodization forms a compact layer that is a mixture of crystalline and amorphous oxide [Habazaki et al., 2003], a post-synthesis heat treatment step is required to induce the amorphous to crystalline transformation. Therefore, the stability of the nanotube structure, and its ability to maintain the tubular morphology through thermal processing was investigated.



Figure 3.18. As-grown and heat-treated samples of nanotubes formed at 20V anodization. The heat-treatment was carried out in an open-air furnace for 3 hours at the temperatures specified in the images.

Nanotube samples were heat-treated in an open-air furnace at various temperatures ranging from 180°C to 750°C for a period of 1 to 3 hours. Results show that for a Ti foil anodized at 20V, heat-treatment temperature below 450°C enabled the nanotubes to maintain their morphology. (Figure 3.18) At higher temperatures, 600°C and above, a coarsening effect occurs during the amorphous to crystalline transformation and the nanotube structure is destroyed. Instead of tubular structures, a densely packed fibrous oxide layer is present after the sample was placed in the furnace at 600°C. In some areas of the image, the outline of the tube morphology is still visible. At 750°C, the oxide is now entirely composed of larger nanoparticles (approximately 100 nm) that appear interconnected, as well as micron-size crystals that have nucleated within the nanoparticle network. As the pore/tube opening closes up due to the growth and coarsening of crystalline grains, the nanotube length also decreases. A nanotube sample that was originally 2 microns in length was reduced to 0.5 microns after 3 hours of anodization at 750°C. In short, the nanotube structure is stable at room temperature, and up to temperatures of approximately 450°C. At higher temperatures, the tube morphology breaks down into nanoparticles.

The identity of the oxide and an examination of the crystalline transformation and its effect on the change in morphology will be discussed in Chapter 4, when characterization of the nanotube structure and composition is covered.

Chapter 4

Characterization of Nanotube Composition and Structure

To fully understand the identity and structure of the nanotubes that result from electrochemical synthesis, characterization of the oxides' composition and crystal structure were performed. The nanotube's oxide composition were examined using energy dispersive xray spectroscopy (EDX) and electron energy loss spectroscopy (EELS). Identification of the crystalline nature of the nanotubes were performed with micro x-ray analysis, using a synchrotron radiation source, as well as high-resolution TEM analysis. Insights into the crystal structure and composition of the different oxides making up the tube morphology provide valuable information in regards to the nanotube formation and growth processes.

4.1 Nanotube Morphology and Fine Interface Features

Cross-sectional transmission electron microscopy (TEM) analysis allows the examination of fine features of the nanotubes and the interfaces between the tubes and the metal substrate, which could give insights into the nanotube's growth mechanism. The cross-sectional images in Figure 4.1 suggest that the tubes, as grown, are always oriented perpendicular to the metal surface. This provides multiple implications for future device engineering. For example, using a cylindrical Ti wire, one can grow radially oriented nanotubes. Similarly, a prepatterned substrate with grooves or trenches might allow for the growth of horizontally aligned nanotubes. By simply pre-processing the Ti substrate prior to anodization, one can promote nanotube growth not only in specific areas but also in predetermined directions.

In addition, the TEM images clearly reveal the presence of a very thin sculpted bar-



Figure 4.1. Cross-sectional TEM images of the nanotubes, giving a clear indication of the barrier oxide layer(identified by arrow), tube wall, and ridges connecting adjacent tubes.

rier oxide layer, approximately 5-10 nm thick, between the tube and the metal substrate (Figure 4.1b arrow). The image shows that the barrier layer is sculpted not only along the tube/barrier interface, but also along the barrier layer/metal substrate interface. The presence of the sculpted barrier layer, directly coating the metal substrate, has on occasion been missed and mistakenly identified as the titanium substrate itself. [Macak et al., 2005a] The importance of identifying the barrier layer and characterizing it is two-fold. One, because the barrier layer appears between the Ti substrate and the nanotubes, it represents an intermediate state of the oxide, before it is converted to the form present in the nanotubes. Therefore, determining the composition and structure of this barrier oxide layer could lead to a better understanding of the nanotube formation mechanism. Two, if these tubular structures are to be used in devices, then electron transport through the nanotubes, as well the barrier layer must be considered, since the barrier layer is in the electron's path on the way to the Ti substrate (which can act as the current collector). The composition and properties of the barrier layer are important to the nanotube characterization effort.

Another notable observation from the TEM images is that the barrier layer thickness is approximately the same size as the ridges/filaments that connect adjacent tubes, appearing periodically throughout the length of the nanotubes. The periodicity of these ridges have been linked to periodic spikes in the current density of the foil sample during anodization. [Macak et al., 2005a] The current fluctuations are attributed to localized changes in concentration and pH that occur inside the tube during growth. In particular, the fluctuations associated with bursts in anodization, which decreases the local pH (according to Equation 1.1), and consequently cause enhanced dissolution by fluoride. The results suggest that the filaments, which appear not only to connect the tubes, but also run across the outer diameter of the tubes, represent the growth fronts during electrochemical synthesis. What was once the barrier layer is converted to the filament oxide, as tube grows into the Ti substrate.

4.2 Nanotube Crystal Structure

4.2.1 Common Titania Structures

Titania exists in three main polymorphs: anatase, rutile and brookite. While compositionally the same (all are TiO₂) they each represent a different arrangement of atoms, making up different crystal structures. Figure 4.2 and Table 4.1 contain the detailed crystal structure and properties data for the 3 phases. Rutile is the thermodynamically stable structure as it has the lowest free energy configuration under standard conditions, while anatase and brookite are metastable. [Fahmi et al., 1993; Navrotsk and Kleppa, 1967] Brookite is also the least common of the three structures, and is mostly found as a natural mineral. Rutile and anatase, on the other hand, appear more often in lab synthesized materials and in many device applications involving titania.



Figure 4.2. Common titania crystal structures. [Mo and Ching, 1995]

Both anatase and rutile have a tetragonal crystal structure composed of Ti-O octahedra, where the Ti core is surrounded by 6 oxygen atoms. In the rutile structure, the octahedra share sides, while in the anatase structure, they share corners. (Figure 4.2) Brookite, in comparison, has an orthorhombic crystal structure. Because rutile is the thermodynamically stable configuration, when heat-treated, both anatase and brookite spontaneously convert to rutile. The anatase to rutile transformation typically occurs in the temperature range of 700°C to 1000°C, depending on crystallite size and impurity content. [Banfield et al., 1993] The phase transformation also results in a volume change, specifically volume shrinkage of

		Duth	A i b	
	Titanium ^{<i>a</i>}	Rutile ^o	$Anatase^{o}$	Brookite ^c
Crystal Structure	hcp	tetragonal	tetragonal	orthorhombic
Lattice Constants (Å)	a = 2.9508	a = 4.594	a = 3.784	a = 9.184
	c = 4.6855	c = 2.959	c = 9.515	b = 5.447
			c = 5.145	
Space Group	P63/mmc	$P4_2/mnm$	$I4_1/amd$	Pbca
Molecule/cell	6	2	4	8
Ti–O Bond Length (Å)	-	1.949(4)	1.937(4)	1.87 - 2.04
	-	1.980(2)	1.965(2)	
O–Ti–O Bond Angle	-	82.1°	77.7°	$77.0^{\circ}-105^{\circ}$
	-	90.0°	92.6°	
Density (g/cm^3)	4.51	4.13	3.79	3.99
Band Gap (eV)	-	3.2^d	3.0^d	1.9^{e} - 3.4^{f}
^a Pawar and Deshpande [1968]				

Table 4.1. Crystal Structure Data and Properties

^a Pawar and Deshpande [1968]

^b Cromer and Herrington [1955]

 $^{c} Baur [1961]$

^d Kavan et al. [1996]

^e Zallen and Moret [2006]

^f Koelsch et al. [2002]

8%, since rutile has a more compact atom arrangement. The difference in their structure leads to a difference in properties as well, with rutile being higher in density, and having a bandgap energy value that is 0.2eV lower than that of anatase. [Kavan et al., 1996]

4.2.2 Micro X-ray Diffraction Analysis

To examine the crystal structure of the nanotubes and the barrier layer the microdiffraction beamline at the Advanced Light Source (ALS), BL 12.3.2 was used. The micro-XRD beamline is unique as it allows the beam size to be focused down to 1x1 micron, allowing for structural characterization with very high spatial resolution. The experimental setup is composed of a monochromated beam (6 keV) of synchrotron radiation striking the sample at a very low grazing angle (0.5°). At this prescribed grazing angle, assuming 60% porosity of the TiO₂ layer, a 6 keV beam has an attenuation length of 0.18 microns (the depth into the material where the beam intensity falls to 1/e of its value). Thus, the x-ray only penetrates the surface of the sample, and the information collected by the CCD detector will be primarily from the top oxide layer and not the Ti substrate.

To prepare samples for the beamline, the nanotube layer from an anodized Ti foil sample was mechanically removed from one edge of the sample, which left just the barrier oxide layer on the surface. Figure 4.4 shows the side view and top view of the nanotubes and the area



Figure 4.3. The experimental set-up for BL 12.3.2 at the Advanced Light Source



Figure 4.4. (a) Side view and (b) Top view images of the XRD sample.

where the nanotubes have been removed. The topview image in Figure 4.4b indicates that the area of exposed barrier oxide in the experiment (dark gray region) was approximately 300 to 400 microns. Data sampling was performed across the surface of the sample via scanning with a 2x5 micron, 6 keV monochromated beam. (Although the beam could be focused down to 1x1 micron, a 2x5 micron beam size was used in order to have sufficient beam intensity for data collection.) By comparing the diffraction pattern from the 2 different areas on a sample, the diffraction peaks from the various oxide layers can be resolved.

Two different types of samples were examined in the study. As-grown nanotube samples, as well as those that have been heat-treated in an open-air furnace at 450° C for 3 hours. The heat-treatment temperature was chosen based on previous stability experiments, which showed that this is the highest temperature at which the nanotubes were able to maintain their tubular morphology. In addition, previous work indicated that 450° C should be a sufficiently high temperature for inducing an amorphous to crystalline transformation in the nanotube structure. [Varghese et al., 2002]



Figure 4.5. Two-theta vs. Intensity plots of as-grown and heat-treated nanotube samples. "A" refers anatase peaks, "R" refers to rutile peaks, and "Ti" marks titanium peaks.

Figure 4.5 shows the diffraction pattern of an as-grown nanotube sample and one that has been heat-treated. The as-grown sample only exhibits Ti peaks, indicating that the top oxide layer has no structural identity, and is amorphous in nature. This is in agreement with other published results. [Varghese et al., 2002; Tsuchiya et al., 2005a; Lee et al., 2006b] Once heat-treated, the nanotube layer contains both anatase and rutile crystal structures, as diffraction peaks for both phases appear in the XRD spectrum. The higher intensity of the anatase peaks compared to the rutile peaks suggests that the mixture is mostly anatase however. The most compelling results come from analyzing the diffraction patterns of the barrier layer and nanotubes in a heat-treated sample. In the nanotube's diffraction pattern, as mentioned, there are strong anatase and weak rutile peaks. In the spectrum for the barrier layer, the anatase peaks are absent, and only the rutile and Ti peaks are present. These result suggest that the sculpted barrier oxide layer in a heat-treated sample is composed entirely of rutile TiO₂, while the heat-treated nanotubes could be a mixture of anatase and rutile.

The x-ray diffraction pattern of the nanotube sample can be used to estimate the percentage of anatase and rutile crystals that are present by comparing the relative intensities of the main anatase and rutile diffraction peaks. Typically, the diffraction peaks used for analysis are $2\theta \approx 26^{\circ}$ for the (101) plane of anatase and $2\theta \approx 28^{\circ}$ for the (110) plane of rutile. The following equation:

$$x_A = \frac{1}{1 + K(I_R/I_A)} \pm 2\%$$
(4.1)

proposed by Criado and Real [1983] will give the fraction of anatase (x_A) present in a sample. In the equation, I_R and I_A are the intensities of the reflections for the (110) plane of rutile and the (101) plane of anatase, respectively, and they are equaled to the total areas of the diffraction peaks. The constant K is a number determined by plotting the values of I_R/I_A , calculated from the x-ray patterns of a series of binary mixtures of both anatase and rutile, as a function of x_R/x_A . This results in the expression: $I_R/I_A = \frac{1}{K} (x_R/x_A)$, adapted from work by Chung [1975], which combines with $x_R + x_A = 1$ to give Equation 4.1. The values of K vary from 1.26 [Spurr and Myers, 1957] to 1.29 [Hubbard et al., 1976], to 2.18 [Criado and Real, 1983], depending on the processing history of the sample. Using an average of these values, K = 1.58, the fraction of anatase in the nanotubes is estimated to be $89\pm 2\%$



Figure 4.6. 2D diffraction ring patterns for the (a) as-grown and (b) heat-treated nanotube samples. Ti, R, and A marks the main diffraction rings belonging to titanium, rutile and anatase structures.

The 2-D XRD ring patterns obtained from the experiments provide additional crystallographic information. (Figure 4.6) Each spot on the diffraction ring belongs to a single crystal/grain, as each grain has only one lattice plane that meets the Bragg condition. Each ring in the pattern represents all the grains whose lattice planes meet the specified Bragg condition, rotated at all angles about the incident beam. Each different lattice spacing produces a spot at a different distance from the center. With an approximate infinite number of grains, at all different orientations and rotation angles about the incident beam, a ring is created for every possible Bragg reflection. Therefore, for a nice, evenly distributed diffraction ring pattern, there must be enough grains within the incident beam spot size and they must be randomly oriented. Spotty diffraction rings indicate that large grains are present in the sample. Brighter regions on the diffraction ring implies that the sample contains more grains in that orientation than in the others.

From comparing the patterns of the as-grown and heat-treated samples, we see a change in the grain structure of the Ti substrate. Heat treatment causes the Ti smooth ring pattern to change into small diffraction spots along the rings radii. The result suggests that grain coarsening had occurred in the sample, where initially fine grains grew into larger grains during heat treatment. The diffraction ring for the (101) plane of anatase indicate that the anatase crystals are small, fine crystallites, randomly oriented. (The anatase grains must be nanocrystalline to yield such a pattern, given that the beam size was only 2x5 microns.) For rutile, instead of exhibiting a ring pattern, the reflection mainly shows up as one broad spot along the (110) plane, indicating that rutile is present as nanocrystals that are textured, yielding a preferential orientation.

4.2.3 High-Resolution TEM

As-Grown Nanotubes

Information about the structure of the nanotubes and their corresponding interfaces is also made available through cross-sectional high-resolution TEM analysis. Although the XRD results suggest that the as-synthesized samples are entirely amorphous, high-resolution TEM images show that the barrier layer oxide is actually semi-crystalline in nature (Figure 4.7). While most of the oxide is indeed amorphous, there are small areas of crystallinity embedded within the amorphous matrix. Albu et al., have also reported the presence of small crystallites in the as-synthesized structures of "double-walled" nanotubes that were formed at a much higher anodization voltage of 120V [*Albu et al.*, 2008]. In this case, the nanocrystals, identified as anatase, are found in the tube wall, which range from 25 to 75nm in thickness. The crystalline regions present in the barrier oxide of our specimen are too small to generate digital diffractograms that can be indexed. Similarly, selected area diffraction (SAD) of the specimen reveals broad, diffuse rings, indicative of an amorphous material, but contains no information on the crystallites. The diffraction spots present belong to the Ti substrate, which has a hexagonal close-packed structure. (Figure 4.7)

What is clear is the contrast seen between the barrier layer oxide and the nanotube oxide (Figure 4.1, suggesting that they are distinct phases. Contrast seen in TEM images can likely be attributed to thickness differences, or a disparity in atomic scattering. In this case, thickness fringes are not probable given the repeat appearance of the very slim, sculpted interface barrier layer throughout various sections of the sample. Thus, the atomic scattering factors of the two oxide layers are assumed responsible for the observed contrast. Since both the nanotube and barrier layer oxides are mostly amorphous, the contrast is attributed to a difference in oxide stoichiometry [*Fultz and Howe*, 2002]. The barrier layer



Figure 4.7. High-resolution TEM image of the Ti substrate, barrier layer, and nanotube oxide. The selected area diffraction pattern shows broad diffuse rings from the nanotubes and diffraction spots from the Ti substrate.

could contain titanium ions of an intermediate oxidation state between zero and Ti^{4+} , or have higher concentrations of Ti^{4+} atoms than the nanotube oxide, forming a TiO_{2-x} phase.

Heat-Treated Nanotubes

The cross-sectional TEM image of the nanotube structure after heat-treatment is shown in Figure ??. The sculpted interface is still maintained, although the thickness of the barrier layer oxide has increased from 5-10 nm to approximately 40-50 nm after 3 hours of heattreatment at 450°C. This explains the strong rutile peak that was seen in the barrier layer XRD pattern, which is more consistent with a 50 nm thick oxide layer than one that is 10 nm. The barrier layer oxide could have thickened due air oxidation of the Ti substrate during heat-treatment, which would require transport of oxygen through the oxide. The shortest transport path is at the bottom of the tube, allowing this area to oxidize the fastest. Thus, the presence of the sculpted metal/oxide interface is still maintained after heat-treatment.

All but one of the nanotube crystals examined in the heat-treated TEM samples were identified to be anatase. Figure 4.9 shows the phase contrast image of an anatase crystal in the tube wall. The anatase crystals appeared slightly textured, with the digital diffractograms from different crystals yielding the same pattern. The crystals, tens of nanometers in size, were mostly aligned in the [010] zone axis. The rutile structure was seen in only one of the many crystals examined in the tube oxide region. This is not surprising given the XRD results, which indicate that the crystalline mixture in the nanotubes is primarily



Figure 4.8. Cross-sectional TEM image of a heat-treated nanotube sample.

anatase (89% or more). The lone rutile crystal in the tube oxide was indexed to be aligned in the [113] zone axis. (Figure 4.9)

High-resolution TEM images of the heat-treated barrier layer also corroborated the XRD data, which showed that the barrier layer oxide is composed of entirely rutile. (Figure 4.11 Multiple regions of the barrier layer were examined and all were identified to be rutile in structure. Moreover, the rutile crystals in the barrier layer were highly textured, with all of the crystals' digital diffractograms yielding the same pattern. These rutile structures were indexed to be in the [001] zone axis. The spots in the diffractograms are elongated, suggesting that the rutile crystal has a range of lattice spacings in the direction of the elongation. The variation of lattice spacing in the [020] direction affectively smears the spot pattern. This is indicative of a strain effect in the crystal. A slight mismatch between the crystal's diffractogram pattern with the rutile reciprocal lattice also suggests that barrier layer crystals are in tension in the (100) plane. Given the similarity between the dimensions of the Ti {1010} planes and the (100) plane of rutile, it is easy to see how the Ti substrate could influence the growth orientation of rutile. (Table 4.1) Indeed, the rutile crystals being in the [001] zone axis orientation indicate that their (100) plane is in contact with the Ti substrate. The dimensions of the planes are not an exact match however, with the Ti's hep



Figure 4.9. High-resolution images of the nanotube wall, showing its crystalline nature after heat-treatment. Image (a) is the phase contrast image of an anatase crystal ([010] zone axis), while image (b) is of a rutile crystal in the nanotube wall ([113] zone axis).



Figure 4.10. A high resolution TEM image of the barrier layer oxide after heat treatment. The digital diffractogram of the crystal shows that it is rutile, with a [001] zone axis orientation.

structure having a slightly larger c lattice constant (4.6855 Å) than the a lattice constant of

rutile (4.594 Å). Therefore, atoms in the (100) planes of rutile are slightly stretched, putting the plane in tension. This data shows that the presence of the Ti substrate influences the direction of the rutile nucleation and growth in the barrier layer oxide, which suggests a surface nucleation mechanism for rutile formation.



Figure 4.11. Phase contrast image of a single anatase crystal in the nanotube wall and the filament oxide connecting adjacent nanotube structures.

Even after heat-treatment, the filaments that connect nanotube to nanotube are maintained. The filaments are also crystalline, and appear to be an extension of the nanotube oxide. The image in Figure 4.11 shows a single crystal extending from the nanotube wall into the filament. Because the nanotube and filament oxide are composed of the same single crystal in many cases, this implies that electron transport can occur not only down the length of the nanotube, but also from tube to tube as they are connected by semiconducting oxide.

4.2.4 Titania Crystallization Kinetics and Phase Stability

Rutile is the thermodynamically stable phase of titania, and anatase crystals that are heat-treated to a sufficiently high temperature will undergo a spontaneous, metastable-tostable irreversible phase change. The transformation temperature has been found to be dependent on the anatase crystallite size and impurity content. [Banfield et al., 1993] The crystallization of amorphous material, or the transformation of one crystalline phase to another, typically happens through a nucleation and growth process. The thermodynamic driving force for the reaction is provided by the Gibbs free energy difference between the two phases considered, which is composed of the volume energy (G_v), surface energy (γ), and strain energy (G_s) terms[Porter and Easterling, 1981]:

$$\Delta G = -V\Delta G_v + A\gamma + V\Delta G_s \tag{4.2}$$

where A is the area of the interface and V is the volume of the nucleating solid. Kinetically, it has been found that the rate of transformation and grain coarsening during the phase change is related to crystallite size. [Gribbs and Banfield, 1997; Banfield et al., 1993] Specifically, the rate of the polymorphic anatase to rutile transformation increases when the starting anatase crystals are nanocrystalline. The transformation rate being a function of the average crystallite size indicates that the increase in available nucleation sites is likely the reason for the rate increase. Indeed, Shannon and Pask [1965] examined the anatase to rutile transformation in single crystals and reported that rutile nucleated at the surface of anatase particles. The proposed mechanism for the phase change involves a minimal redistribution of cations and anions within a relatively unchanged oxygen lattice. Therefore, with smaller crystals, more surfaces are available for nucleation to occur, and the transformation rate increases.

The anatase crystals must achieve a critical nucleus size (proposed to be 10-20 nm) before it can transform to rutile [Banfield et al., 1993], and therefore in crystalline mixtures of anatase and rutile, the rutile crystals tend to be larger in size than their anatase counter parts. Kumar et al. [1993] reported that once the anatase to rutile transformation starts to occur in a sample, the size of the rutile crystals are at least 30nm larger than anatase crystallites in the same sample. This observation has led to studies and experimental results that support the theory of anatase being more stable than rutile at small crystallite sizes. [Gribbs and Banfield, 1997] The reversal of stabilities is attributed to rutile having a higher surface energy than anatase. As Equation 4.2 shows, the change in surface energy associated with a phase transformation is an important contribution to the driving force. Gribbs and Banfield [1997] used thermodynamic data and theoretical modeling to show that a 15% greater surface energy for rutile causes the total free energy for rutile to be larger than anatase at crystallite sizes in the nanometer range. As such, titania crystals with diameters in the few nanometer range tend to be anatase.

Understanding this subtlety of titania phase stability allows for clear interpretation of the nanotube crystalline data. After heat-treatment at 450°C, the nanotubes are mostly composed of nanocrystalline anatase, with a small amount of rutile. The barrier layer however is composed entirely of rutile. It can be assumed that during heat-treatment, as the amorphous to crystalline transformation occurs, the initial crystals that nucleate are anatase. The thickness of the nanotube wall (5 to 20 nm, depending on the location along the tube length) limits the size of the anatase crystals that can form, and therefore suppress their transformation to rutile. The critical nucleus size required for rutile formation is generally not reached inside the nanotube wall. (However, a small amount of anatase crystals do reach the critical size and transform to rutile, providing the small rutile signals that we see in our samples.) In the barrier layer, where there is no lateral constraint on the size of the crystals, as the barrier layer expands over the entire surface of the substrate, rutile transformation can and does take place. In addition, the presence of the Ti substrate affects the orientation of the rutile crystals, as discussed in Section 4.2.3. We found that the rutile formed in the barrier layer oxide have a preferred crystallographic orientation. Because the titanium substrate appears to influence crystal orientation in the barrier layer oxide, suggesting that rutile crystals are nucleating at the oxide/titanium interface, and adopting an orientation that allows for minimum lattice mismatch between rutile and titanium's hcp structure.

Besides inducing the crystallization transformation, high temperature heat-treatments also affect nanotube morphology. As reported in Chapter 3, the heat-treatment has an adverse effect on the stability of the nanotube structure, particularly at high temperatures. The breakdown of the tubular morphology at elevated temperature is likely due to enhanced mobility of the atoms and mass transport rate, which results in solid-state sintering. [Kumar et al., 1995; Varela et al., 1990; Whittemore and Sipe, 1974] Enhanced sintering and the reduction in porosity of a structure is an example of the Hedvall effect [Kumar, 1995], which states that if a material undergoes second-order phase transition, thermally activated processes at its surface may show anomalies in their reaction rates. [Seifert and Dietrich, 1987. The enhanced mobility of ions at the oxide surface leads to sintering of nanotubes and subsequent grain growth and densification, effectively destroying the tubular structure that results from electrochemical synthesis. The reduction of porosity in the oxide after heattreatment, along with the decrease in oxide layer thickness (from 2 microns to 0.5 microns after 3 hours at 750°C) supports the theory of enhanced mass transport rate. The nanotube oxide layer essentially collapses at high heat-treatment temperatures. The sintering effect in the nanotubes appears to occur at temperatures higher than 450° C, as heat-treatment below this temperature allowed maintenance of the tube morphology to a certain degree.

Another factor that could affect the stability of the nanotube morphology is the nucleation and growth of rutile crystals. It has been established by multiple studies that rutile crystals tend to be larger than anatase. [Kumar, 1995; Kumar et al., 1993; Lin et al., 1994] Once rutile nucleates and grows, the crystal diameter can exceed the initial tube wall thickness and contributes to the reduction of the internal volume of the nanotube, and therefore the sample's porosity. Lin et al. [2003] examined the stability of titania nanotube structures and found that at higher temperatures, the percentage of rutile crystals increases and the porosity of the oxide decreases. The transition from mostly anatase to mostly rutile in nanotubes grown at 20V occurs at approximately 580°C. At temperatures higher than this, the structure is almost entirely rutile, and the oxide is composed of jagged crystals, hundreds of nanometer in size or larger, similar to that seen in the nanotube sample heat-treated at 750°C (Figure 3.18). These observations lead to the conclusion that in order to maintain the nanotube morphology at high temperatures, both sintering effects and the anatase to rutile phase change need to be limited. One way this can be accomplished is via addition of impurities, such as those with valencies greater than 4^+ , that can slow the rutile to anatase transformation [Banfield et al., 1993; Shannon and Pask, 1965]. The addition of rare earth metal oxides has also been found to impede the anatase to rutile transformation, by suppressing the nucleation of the transformation. [Hishita et al., 1983]

4.3 Oxide Composition

Compositional analysis of the nanotube samples were performed via analytical electron microscopy (AEM) techniques. Specifically, energy dispersive x-ray spectroscopy (EDS), and electron energy loss spectroscopy (EELS) were used to probe the composition of the nanotube oxide, the filament oxide, and the barrier layer oxide. Both EELS and EDS techniques use inelastic scattering of a high energy electron beam (e.g. 100keV) by a thin specimen. Atoms within the specimen are ionized by the incident electron beam and their core electrons are ejected. When electrons from the outer shells move in to occupy the newly empty states, they emit characteristic x-rays with energies equaled to the energy difference between the outer and inner shells. EDS utilizes these characteristic x-rays to determine the sample's chemical components. EELS on the other hand measures the energy loss by the incident electrons after their interaction with the sample (inelastic scattering). The energy losses are characteristic of the elements and chemistry of the specimen, and thus can be used to determine the elemental components of a sample, among other information. While these techniques are useful for determining material composition, they both have their drawbacks. For EDS, the generation efficiency of characteristic x-rays vary with the atomic number (Z) of the elements, with lower yield at lower atomic numbers. The technique is not good for examining light (lower Z) elements, specifically elements with Z < 10. EELS, by nature, tends to have a poor signal to background ratio, which makes data interpretation more difficult. Combining both analytical techniques provides more complete and balanced information about the nature of the different nanotube oxides.

4.3.1 Energy Dispersive X-ray Spectroscopy

As-Grown Nanotubes

EDS analysis supports the hypothesis that the nanotube and barrier oxides have differing compositions. Figure 4.12 shows a line-scan performed over the nanotube, barrier layer, and titanium substrate, while Figure 4.13 presents individual spot scans of these three areas.

Both the line-scan and spot scans indicate similar results, that the barrier layer oxide has higher concentration of titanium and lower concentration of oxygen than the nanotube oxide. It is worth noting that the ratio of intensities of Ti/O of the nanotubes is significantly



Figure 4.12. EDS line-scan performed over the length of the nanotube, the barrier layer and the titanium substrate on an as-grown sample. The insert is an expanded view of the oxygen and fluoride concentrations.



Figure 4.13. EDS spot scans of an as-grown nanotube sample in the 3 regions of the interests: the nanotube wall, the barrier layer, and the titanium substrate.

greater (about 4x) than that of the barrier layer. The lower value of the ratio for the barrier layer is consistent with the previously stated inference, drawn from differences in contrast of the nanotubes and barrier layer seen from TEM images, that the barrier layer is depleted in oxygen relative to the nanotubes. Both the nanotubes and barrier layer also have some small incorporation of fluoride ions, which drops off to zero in the Ti substrate. However, there is no evidence of F^- enrichment at the oxide/metal interface, as reported by *Habazaki et al.* [2007] for the high- voltage anodization (100V or higher) of Ti in fluoride-containing electrolytes. Instead, the fluoride signal intensity is constant throughout the oxide and decreases as the scan enters the metal, which is similar to the XPS depth profile data reported by *LeClere et al.* [2008]. The incorporation of fluoride ions into the oxide could affect the oxides defect structure, and therefore its electronic properties. Although EDS provides useful qualitative data and indication of trends, it cannot be relied on for quantitative analysis of light elements, such as oxygen (Z=8) [*Fultz and Howe*, 2002]. As such, while the compositional elements of the nanotube and barrier layer oxides are known, the exact identity of the oxide in the as-grown state remains unclear.

Heat-Treated Nanotubes

Similar results were seen in nanotube samples that were heat-treated at 450°C for 3 hours. Figure 4.14 shows the region of the sample over which the line-scan was performed, while Figure 4.15 shows the EDS data. After heat-treatment, the fluoride signal is no longer present in the EDX scan. The oxygen and titanium signals throughout the nanotube, the barrier layer and the titanium substrate, however, mirror the pattern that was seen in the as-grown case. Once again, the oxygen signal in the barrier layer is smaller than that in the nanotube oxide. The thickness of the barrier layer increases to 40-50 nm after heat-treatment, which allows for multiple points of analysis within this region. This is in contrast to the as-grown case, where the barrier layer is so thin (5-10 nm) that only one data point could be taken from the area during the line-scan. In addition, the increased thickness of the oxide layer also ensure that the information obtained is not an artifact of a slanted interface, where there might be an overlap of the Ti and oxide regions. The change in oxygen and titanium concentration as the scan moves from the nanotube/barrier layer interface into the barrier layer and eventually the Ti substrate indicates that there is a compositional gradient within the oxide.

4.3.2 Electron Energy Loss Spectroscopy

EELS analysis allows for elemental mapping of the sample, showing the spatial distribution of different elements of interest. This is accomplished by filtering the energy-loss electrons collected by the detector so that only those with particular energy values are captured. In this analysis, the chemical elements of interest are titanium, oxygen, and fluoride,



Figure 4.14. Image of the region in the heat-treated sample where EDS line-scan was performed over the length of the nanotube, the barrier layer and the titanium substrate.



Figure 4.15. EDS linescan data of the region in Figure 4.14



Figure 4.16. The EELS elemental maps of titanium, oxygen, and fluoride in heat-treated nanotube samples.

corresponding to energy-loss values of 456 eV (Ti L-edge), 532 eV (O K-edge) and 658 eV (F K-edge).

Energy filtered images of the heat-treated nanotube samples are presented in Figure 4.16. In each of the elemental map images presented, regions with higher concentration of the target element show up brighter than areas that do not contain the element. The results indicate that the oxide layer adjacent to the Ti substrate contains less oxygen than the nanotube oxide, corroborating the results seen in EDX analysis. The Ti map however does

not show clear differences in the concentration of Ti in the barrier layer and the nanotube oxide. Whatever differences there are, they are minimal and not discernible. The F map image, which has gone through digital enhancement to make the weak fluorine signal visible, suggests that there is fluoride incorporation in the nanotube and barrier layer oxides. Most of the fluoride however appears in the nanotube oxide. There is also a slight increase of the fluoride signal at the interface between the barrier layer and the metal substrate. These results suggest that fluoride incorporation, however is small, so that it does not get picked up in the EDX analysis. As mentioned, EELS is more sensitive to lighter elements (Z<10) than EDX, and fluoride (Z=9) is close to the EDX detection threshold.

Chapter 5

Insights on Nanotube Growth Mechanism from Growth and Characterization Experiments

5.1 Electrochemical Experiments

Results from electrochemical synthesis experiments indicate that nanotube growth is sensitive to the electrolyte chemistry. In addition to the applied potential, changes in pH, solvent, and anions in solution will affect the growth process and yield nanotubes with varying morphology.

Synthesis experiments examining the effects of different anions such as Cl^- , Br^- , and $F^$ on nanotube growth reveals valuable information about the nature of nanotube formation. Results indicate that nanotube growth in Cl^- and Br^- solutions occurs within pits on the substrate surface, while growth in fluoride containing solution do not occur due a pitting effect. Nanotubes that form in F^- -based solution appear homogenously and uniformly over the entire surface of the substrate. This is in contrast with what is seen with Cl^- , $Br^$ solutions, where the nanotubes appear in bunches, in pitted regions. Experiments looking at the progression of nanotube growth with synthesis time confirms that the growth process occurs simultaneously over the entire surface of the substrate, and the transformation from a planar oxide surface to a porous one occurs over a matter of seconds.

The pitting mechanism proposed for nanotube formation in F^- electrolytes is further debunked with experiments involving nanotube growth on substrates with pre-formed "pits" on the surface. The presence of pre-existing pits/dimples on the surface of the oxide did not affect the growth process, which appears to include a distinct initiation step, where nucleation of the pores occur, followed by the growth step. Similarly, using a substrate with pre-existing, fully formed nanotubes on the surface did not affect the growth process. Again, a nucleation step is required before nanotube growth can commence.

Most notably, results from interrupted growth tests, where the anodization process was stopped for 30 seconds to 5 minutes before being resumed, show that the electrolyte chemistry inside the tubes is of particular importance and is likely very different from the bulk electrolyte during growth. It is the maintenance of the unique electrolyte chemistry inside the tube, near the oxide/electrolyte interface, that enables nanotube growth. As such, a pause of 30 seconds allows nanotube growth to continue uninterrupted, while a long pause of 5 minutes require the formation of a new layer of nanotubes. (Figure 3.17)In the second instance, with a 5 minute pause, the electrolyte composition inside the nanotube is no longer what is required for growth and a nucleation process proceeds before nanotube growth can occur.

Taken together, the electrochemical experiments reveal that the nanotube formation process includes two primary steps: pore nucleation and pore growth. Pore nucleation is a global process (Figure 3.6) which occurs simultaneously and homogeneously over the entire surface of the metal substrate. Pore growth is a dynamic process that involves both the oxidation of metal and dissolution of already formed oxide. The chemistries at the oxide/electrolyte interface, near the tube bottom where oxide growth is occurring, are important factors dictating nanotube growth. The initial morphology of the oxide surface, on the other hand, is less important. The presence of a dimpled/sculpted oxide surface is not enough to promote nanotube growth, and neither is the presence of already formed nanotubes. In both these cases, a nucleation steps is required before growth conditions could be established, allowing nanotube growth to occur.

The conditions under which a planar surface transforms into one with nucleation occurs is again affected by the chemistries and compositions near the oxide/electrolyte surface. While the importance of the electrolyte chemistry is highlighted in the synthesis experiments, information on the chemistry of the oxide is revealed through structural and compositional analysis.

5.2 Structural and Compositional Analysis

Structurally, the cross-section of an electrochemically synthesized nanotube sample reveals that the nanotubes grow on top of a thin, sculpted barrier layer oxide that covers the surface of the metal substrate. This barrier layer is about 5-10 nm thick in the as-grown state, and increases to 40-50 nm after a 3 hour heat treatment at 450°C. Compositional analysis indicate that the barrier layer oxide and the nanotube oxide have differing Ti^{4+} and O^{2-} compositions, with the barrier oxide being deficient in oxygen/enriched in titanium. The Ti/O ration of the barrier layer is 4x more than the ratio of the two elements in the nanotube oxide. This change in composition from the nanotube to the barrier layer indicate that there is a compositional change in the oxide as we move from the oxide/electrolyte interface to the oxide/metal interface. The presence of a compositional gradient in the growing oxide could be a result of the anodization process, during which oxygen ions are added at the oxide/electrolyte interface. Consequently, at the electrolyte/oxide interface, there is oxygen enrichment and metal ion deficiency while the opposite is true at the oxide/metal interface.

The cross-sectional images also reveal that the nanotubes are connected by oxide filaments that run perpendicular to their growth direction. The oxide filaments appear periodically, in conjunction with current spikes during anodization, suggesting that they are growth fronts during electrochemical synthesis, and that the oxide in the barrier layer is converted to the filament oxide, as the tubes grow into the Ti substrate. The transition from one oxide layer to another requires transport of oxygen from the electrolyte/oxide interface to the oxide/metal interface.

Results from TEM and XRD analysis reveal that the as-formed nanotubes are amorphous, with nanocrystalline regions embedded within the amorphous matrix. The tubular structures can be converted to a nanocrystalline mixture of anatase and rutile, both common phases of titania, with heat-treatment. Once crystallized, the barrier layer is entirely rutile in structure while the nanotubes contain a mixture of anatase and rutile. The difference in the crystal structure of the two layers results from differences in oxide morphology, and not the compositional difference mentioned above. Rutile crystals are present in the barrier layer because crystals that nucleate within the barrier layer can grow to larger size due to the lack of lateral restriction, and as discussed, rutile is the thermodynamically stable phase of titania at large crystal sizes. Within the nanotubes, the thickness of the tube wall limits the size of crystals that form during heat-treatment, and thus the crystals are more likely to be anatase since they cannot achieve the critical nucleus size required for rutile formation. The compositional difference in the two oxide layers, although not related to differences in crystal structure, is likely important during the growth of the oxide.

Overall, results from structural and compositional analysis indicate that along with the composition of the electrolyte, the composition of the oxide plays an important role in the growth of nanotubes.

Chapter 6

Initiation Model for the Formation of Organized Nanotubes/Nanopores

6.1 Nanotube Formation

Nanotube formation is composed of three main steps, the initiation of pores, the growth and elongation of these structures, and the transformation from a porous array to a tubular array. Several fairly detailed mechanisms of pore growth have been proposed, while the initiation steps have not been thoroughly explored. This chapter will introduce a new model of looking at nanopore/nanotube initiation. It is proposed that pore initiation occurs as welldefined process, and is also the start of the organization of nanotubes/nanopore arrays. The pores initiate as a consequence of compositional and potential gradients in the oxide at the oxide/electrolyte interface and capillary effects, which lead to the breakdown of the planar interface into an initially disorganized array of nanopores. The pore organization starts as a consequence of a particular pore diameter/spacing propagating at a rate faster than all others. The fastest-growing pore diameter is a function of the oxide-electrolyte interfacial energy and the gradients of potential and composition in the oxide at the oxide/electrolyte interface.

6.1.1 Growth of Organized Arrays of Nanotubes/Nanopores

Existing growth models indicate that the organization of the nanopore/nanotube arrays occurs in the pore growth stage during the anodization of Al [Jessensky et al., 1998; Garcia-Vergara et al., 2007; Gong et al., 2001] and Ti [Yasuda et al., 2007; Raja et al., 2005; Choi et al., 2004]. A brief summary of the growth-related organization mechanisms is as follows. Jessensky et al. [1998] indicate that mechanical stress, which is associated with the volume difference of aluminum and Al₂O₃, causes a repulsive force between neighboring pores and is responsible for the ordered arrays of pores in alumina formed by anodization of aluminum in 0.3 M oxalic acid and in 20% sulfuric acid. Garcia-Vergara et al. [2007] provide another mechanism of pore growth in aluminum oxide: field-assisted plasticity and flow of material under growth stresses during anodization of Al-3.5 atom % W in 0.4 M sulfuric acid. Parkhutik and Shershulsky [1992] quantitatively modeled the steady-state growth of the aluminum/ barrier layer/porous aluminum oxide structure that was revealed by earlier microscopy investigations. Importantly, the model recognized that the scalloped aluminum/barrier layer interface caused an inhomogeneous electric field in the oxide. The inhomogeneous field- assisted movements of the aluminum/oxide and oxide/electrolyte interfaces maintained pore growth.

A number of authors have also suggested growth mechanisms for organization of nanoporous and nanotubular arrays in TiO₂.[*Tsuchiya et al.*, 2005c; *Yasuda et al.*, 2007; *Gong et al.*, 2001] According to *Yasuda et al.* [2007] the larger volume of oxidizable metal associated with deep pores creates greater acidification of the pore electrolyte, which leads to faster oxide dissolution and pore penetration into titanium. Self-organization is the result of the synergism between oxidation which lowers the pH and thereby enhances oxide dissolution and oxide dissolution which increases metal oxidation. Another theory, proposed by *Raja et al.* [2005], suggests that planar instability induced by strain energy due to compressive stresses from electrostriction, electrostatic forces, and volume expansion leads to the formation of nanopores. As mentioned earlier, the strain energy mechanism is unsupported by experimental data. There is no evidence that higher compressive stresses result in higher adsorption of fluoride ions, as required by the theory.

In summary, earlier mechanisms of the formation of nanoporous structures are composed of two distinct steps, (i) an unspecified pore initiation mechanism operating at unspecified surface defects, followed by (ii) various pore growth mechanisms [*Tsuchiya et al.*, 2005; *Yasuda et al.*, 2007; *Jessensky et al.*, 1998; *Garcia-Vergara et al.*, 2007; *Gong et al.*, 2001; *Raja et al.*, 2005; *Parkhutik and Shershulsky*, 1992] which result in organization of the nanopores. These proposed mechanisms however, disregard for the role of the initiation stage. While the growth mechanisms mentioned all rely on the initial formation of a dimpled or sculpted interface in order to promote pore growth with metal anodization, the initiation stage is only briefly addressed and is attributed to a pitting process at defect sites. As seen by the experimental data in Chapter 3, this mechanism is not sufficient for describing the initiation mechanism, which occurs homogenously and simultaneously across the surface of the oxide. A new theory is needed to explain the initiation and formation of organized arrays of nanotubes and nanopores.

6.2 Mechanism of Initiation

Anodization consists of four steps, which are summarized in the sketches presented in Figure 6.1: (1) oxidation of metal at the metal/oxide interface, e.g., $M \to M^{+z} + ze^{-}$; (2) electrochemical reduction at the surface of the counter electrode, e.g., $O_2 + 2H_2O + 4e^{-} \to 4OH^{-}$; (3) addition of O^{2-} to the oxide at the oxide/electrolyte interface; and (4) migration of M^{+z} from the metal/oxide interface to the oxide/electrolyte interface and migration of O^{2-} from the oxide/electrolyte interface.



Figure 6.1. A schematic diagram showing the four different steps involved in anodization.

The formation of nanopores is related to the localized dissolution of the anodized oxide film. The analysis begins by considering the oxide dissolution reaction as described by Equation 6.1:

$$MO_{z/2} + \frac{z}{2}H^+ \to M^{+z} + \frac{z}{2}OH^-$$
 (6.1)

Processes that contribute to oxide dissolution can be inferred from the equilibrium constant expression for the reaction in Equation 6.1

$$K_D = \frac{[M^{+z}][OH^{-}]^{z/2}}{[H^{+}]^{z/2}}$$
(6.2)

or equivalently by

$$K_D = \frac{[M^{+z}](K_w)^{z/2}}{[H^+]^z}$$
(6.3)
and

$$K_D = \frac{[M^{+z}][OH^{-}]^z}{(K_w)^{z/2}}$$
(6.4)

where K_w is the equilibrium dissociation constant of water and [X] represents the activity of species X and is assumed to be approximately equal to the concentration of X. Processes that either decrease $[M^{+z}]$ or increase $[H^+]$ favor the dissolution of the oxide.

In particular, one direct method of lowering the ratio $[M^{+z}]/[H^+]$ is to lower $[M^{+z}]$ through the action of a complexing agent, such as F^- , in the electrolyte. For example, with sufficient concentration of fluoride, titanium cations in the electrolyte adjacent to the anodized film can be lowered to essentially zero by the reaction represented in Equation 1.2. The addition of fluoride therefore greatly contributes to the dissolution of oxide formed by anodization. What needs to be explained is the localized nature of the dissolution and how it results in the formation of organized arrays of nanopores.

6.2.1 Breakdown of the Planar Oxide/Electrolyte Interface Dur-

ing Dissolution

The most important clue regarding the mechanism of nanopore initiation is the fact that porosity develops in a nearly identical manner across the entire surface of the sample (Figure 3.6). These characteristics of simultaneity and homogeneity are consistent with instability of the planar oxide/electrolyte interface initiating nanopores. The stability of the planar oxide/electrolyte interface during oxide dissolution is dictated by relative gradients of composition and potential in the oxide and electrolyte. When the absolute value of the potential gradient within the oxide decreases below a critical value, determined by the compositional gradient within the oxide, the planar interface is unstable and nanopores initiate. As long as the oxide thickness is uniform across the sample, the potential gradient in the oxide will be the same at every location on the samples surface, as will the compositional gradient in the oxide. Given this condition, the planar interface will become unstable across the samples surface, causing nanopores to form simultaneously across the entire surface.

In the following sections, the variation of composition and the variation of potential in the oxide at the oxide/electrolyte interface are described. The criteria for breakdown of the planar interface and formation of nanopores are then shown to be a consequence of the combined effects of compositional and potential variations in the oxide at the oxide/electrolyte interface.

6.2.2 Variation of Composition in the Oxide and Electrolyte

As described by the following equation, two specific compositional changes occur at the oxide/electrolyte interface during anodization, one in the oxide and the other in the electrolyte:

$$OH_{aq}^- \to O_{ox}^{2-} + H_{aq}^+ \tag{6.5}$$

That is, the electrolyte adjacent to the oxide/electrolyte interface is acidified as O^{2-} are added to the oxide. Simultaneously, the composition of the oxide at the interface is depleted of metal cations, M^{+z} . According to the theoretical analysis conducted, the enrichment of O^{2-} /depletion of M^{+z} in the outer region of the oxide is crucial to the initiation of nanopores. Experimentally, *Taveira et al.* [2005] have reported that, indeed, the concentration of O^{2-} is high and the concentration of M^{+z} is low at the surface of TiO₂ during anodization of titanium. Although there is an excess of oxygen ions in the oxide near the oxide/electrolyte interface, charge neutrality is maintained by the excess of metal cations, M^{+z} , at the metal/oxide interface. This observation is also corroborated by the EDS and EELS results presented in Chapter 4, which show a gradient of oxygen and titanium concentration through the thickness of the barrier layer oxide, leading to oxygen depletion and titanium enrichment near the metal/oxide interface.

The excess cations, M^{+z} , and excess anions, O^{2-} , are initially concentrated at the oxides two interface planes. Diffusion and migration move the cations toward the oxide/electrolyte interface and the anions toward the metal/oxide interface. Given sufficient time, the oxide will tend toward homogeneity. However, after only a short period of time, the excess ions are distributed throughout the two interfacial regions of the oxide as sketched in Figure 6.2. The compositional changes contribute to the destabilization of the planar oxide/ electrolyte interface during oxide dissolution.

6.2.3 Variation of Potential in the Oxide and Electrolyte

The voltage applied during anodization is distributed among potential drops at the metal/oxide interface, through the oxide, at the oxide/electrolyte interface, through the electrolyte, and at the electrolyte/counter electrode interface. The majority of the potential drop however occurs within the oxide. The nature of the potential variation in the oxide depends on (i) the magnitude of the applied potential (i.e., the anodization voltage) and (ii) the distribution of excess cations and anions in the oxide.

When the anodization voltage is zero, the only potential drops occur at the two surfaces of the oxide. The magnitude of these interfacial potential drops is dictated by the assumption that the rate-determining step (RDS) in the growth of the anodized oxide is transport of ions through the oxide. Because the RDS is ion transport, the interfacial charge-transfer reactions are at equilibrium. Consequently, when V = 0, the potential drop between the metal and electrolyte is the equilibrium potential of the anodization reaction, ${}^{M}\Delta^{S}\phi_{e}$. As shown



Figure 6.2. Sketches of the distribution of cations and anions (a) and net charge density in the oxide during anodization (b)

in Figure 6.3, this potential is subdivided between the potential drop at the metal/oxide interface, ${}^{M}\Delta^{OX}\phi_{e}$, and the potential drop at the oxide/electrolyte interface, ${}^{OX}\Delta^{S}\phi_{e}$

$${}^{M}\Delta^{S}\phi_{e} = {}^{M}\Delta^{OX}\phi_{e} + {}^{OX}\Delta^{S}\phi_{e} \tag{6.6}$$

During anodization, V is greater than 0 (i.e., potential of the metal is greater than the potential of the electrolyte), and potential drops occur within the oxide and electrolyte as well as at the two interfaces Figure 6.3. The potential drops within the oxide are affected by the distribution of excess cations and anions, which is described in Figure 6.2. In the absence of space-charge regions, the potential drop through the oxide is linear. Due to the distribution of excess ions in the space-charge regions, the potential varies nonlinearly with distance. The dependence of the anodized TiO₂ film thickness (Δ) on the anodization voltage (V) is such that the gradient of applied voltage though the oxide is steep (approximately 1 V/nm). [Dyer and Leach, 1978] Thus, when initiation of pores occurs, the voltage gradient is well approximated by -V/ Δ , that is, by assuming that the distribution of ions in the film does not significantly affect the distribution of potential. Accounting for the effect of excess O²⁻ in the oxide near the oxide/ electrolyte interface increases the voltage gradient so that, rigorously, V/ Δ represents a lower limit of the voltage gradient in the oxide space-charge



Figure 6.3. (a) Variation in potential across the metal/oxide/electrolyte interphase region when the applied voltage is zero. (b) Variation in potential across the metal/oxide/electrolyte interphase region when the applied voltage, V, is > 0

region. The nature of the potential variation in the oxide has a major effect on the stability of the planar oxide/electrolyte interface and the formation of nanopores.

6.2.4 Criteria for the Breakdown of the Planar Interface and the

Initiation of Nanopores

As is the case for any phase boundary, the macroscopic shape of a moving liquid/solid interface is constantly undergoing microscopic fluctuations, a consequence of the atomic nature of matter. Atomic vibrations produce infinitesimal fluctuations in the values of thermodynamic state parameters such as temperature, pressure, and composition. The submicroscopic fluctuations decay if the original interface shape is stable and grow if the interface is unstable and the fluctuations are of proper size and shape.

Two types of perturbation of the planar interface are possible, positive and negative perturbations. A positive perturbation describes a bump on the surface of the oxide that extends into the electrolyte, while a negative perturbation refers to a depression or dent on the oxide surface, in which the electrolyte moves into the space formerly occupied by oxide. Because our analysis addresses the initiation of planar interface breakdown, the perturbations are considered infinitesimal in size and they do not alter the compositional and potential gradients associated with the planar interface.

The initiation of nanopores/nanotubes requires negative perturbations or dents. These dents on the oxide surface are stable and lead to the formation of nanopores if the driving force for dissolution at the tip of the dent is greater than the equilibrium value that exists at the planar interface. Expressions for the driving force for dissolution are derived based on the variations of composition and potential in the oxide described above. Two criteria for the formation of nanopores are developed, depending on whether the oxide dissolves by electrochemical reductive dissolution or chemical dissolution.

6.2.5 Electrochemical Reductive Dissolution of the Oxide

First, consider the electrochemical dissolution reaction of the anodized oxide. Although many reactions are possible for oxides in F^- containing electrolytes, [*Hepel et al.*, 1982] a fairly general dissolution reaction can be expressed as the following:

$$M_y O_{z/2} + \frac{yz}{2} H^+ + yuF^- + y(z-u)e^- \to y(MF_u)_{aq} + \frac{yz}{2} OH^- + \frac{z(1-y)}{2} O_{OX}^{2-}$$
(6.7)

where z is the oxidation state of M in $M_yO_{z/2}$, u is the oxidation state of M after the electrochemical reduction of $M_yO_{z/2}$ in fluoride-containing electrolytes, and y is the fraction of the stoichiometric concentration of M^{+z} in the oxide near the oxide/electrolyte interface. Last, $(MF_u)_{aq}$ is the aqueous phase complex formed between M^{+u} , and F^- and O^{2-} represents the oxide ions that remain on the surface of the anodized film after the electrochemical reduction of $MO_{z/2}$ in the fluoride electrolyte.

Fluoride is included in the electrochemical reduction reaction in recognition of the experimental observation that specific anions, such as fluoride in the case of a number of valve metals including titanium, tantalum, and niobium are required for the formation of nanopores. [Sieber et al., 2005b; Choi et al., 2006]

The Nernst equation describing equilibrium at the oxide/electrolyte interface is given by:

$${}^{OX}\Delta^{S}\phi_{e} = {}^{OX}\Delta^{S}\phi_{e}^{o} - \left\{\frac{RT}{y(z-u)F}\right\}$$

$$\left\{\left(y\ln[(MF_{u})_{aq}] + \frac{yz}{2}\ln K_{w} + \frac{z/2}{1-y}\ln[O_{OX}^{2-}] - \ln[M_{y}O_{z/2}] - (yz)\ln[H^{+}] - (yu)\ln[F^{-}]\right\}$$
(6.8)

If the potential drop at the oxide/electrolyte interface is greater than ${}^{OX}\Delta^S\phi_e$, then the oxide is stable. If the potential drop at the oxide/electrolyte interface is less than ${}^{OX}\Delta^S\phi_e$, then the oxide is thermodynamically unstable and tends to dissolve. The criterion for breakdown of the planar oxide/electrolyte interface (i.e. the criterion for initiation of nanopores), is derived by introducing a dent in the planar interface and determining whether the dent will grow or shrink. The dent will grow if the potential drop at the oxide/electrolyte interface, ${}^{OX}\Delta^S\phi_e$, at the tip of the dent is less than ${}^{OX}\Delta^S\phi_e$ at the tip of the dent.

The equilibrium value of the potential drop at the tip of the dent is different from its values at the planar interface because the composition of the oxide at the two locations are different. As sketched in Figure 6.4, the equilibrium value of the potential drop across the oxide/electrolyte interface (the vertical dashed line marks the position of the planar interface) increases as the position of the interface shifts to the left. Equation 6.8 indicates that ${}^{OX}\Delta^S\phi_e$ increases because y (the fraction of the stoichiometric concentration of M^{+z}) increases in the direction of negative x, so that the activity of $M_y O_{z/2}$ increases. In other words, the oxide's equilibrium potential, ϕ_e^{OX} , increases with distance from the oxide/electrolyte interface as a consequence of the increase in cation concentration. If a dent forms in the oxide's surface and the tip of the dent is located at x < 0, the equilibrium potential drop at the tip of the dent $[\phi_e^{OX}(x < 0) - \phi_e^S]$ is different from the equilibrium potential drop at the planar oxide surface $[\phi_e^{OX}(x = 0) - \phi_e^S]$.

Also shown in Figure 6.4 are two possible variations of the actual interface potential drop, ${}^{OX}\Delta^S\phi_{actual} = \phi^{OX}(x) - \phi^S$. The value of ϕ^{OX} increases as x becomes more negative because of the polarity of the anodization voltage. The planar interface is at equilibrium, so ${}^{OX}\Delta^S\phi(x=0) = {}^{OX}\Delta^S\phi_e(x=0)$. If ${}^{OX}\Delta^S\phi_{actual}(x) > {}^{OX}\Delta^S\phi_e(x)$ (case A), the oxide is stable a x, the tip of the dent, and the interface remains planar. If ${}^{OX}\Delta^S\phi_{actual}(x) < {}^{OX}\Delta^S\phi_e(x)$ (case B), the oxide phase is unstable at the tip of the dent, allowing the perturbation to grow and causing the planar interface to break down. Thus, the criterion for breakdown of the planar oxide/electrolyte interface during anodization when the oxide dissolves by electrochemical reduction is

$$\partial^{OX} \Delta^S \phi_{actual} / \partial x|_{x=0} > \delta^{OX} \Delta^S \phi_e / \delta x|_{x=0}$$
(6.9)

where both sides of the inequality are negative $(\partial^{OX} \Delta^S \phi_{actual} / \partial x) \delta x$ is the change in the actual value of the interface potential drop as the interface moves into the oxide a distance



Figure 6.4. Variation of the equilibrium potential, ${}^{OX}\Delta^{S}\phi_{e}$, as a function of the position of the planar oxide/electrolyte interface. Also shown with dashed lines are two proposed plots of the variation of the actual potential drop across the oxide/electrolyte interface.

 $\delta x. \ \delta^{OX} \Delta^S \phi_e / \delta x$ does not represent a true differential, because ${}^{OX} \Delta^S \phi_e$ is only defined at the oxide/electrolyte interface, but instead describes the change in the equilibrium value of the interface potential drop as the interface moves a distance δx into the oxide. The value of $\delta^{OX} \Delta^S \phi_e / \delta x$ is primarily dictated by the change in oxide composition with distance from the oxide surface, while $\partial^{OX} \Delta^S \phi_{actual} / \partial x$ is mainly determined by the change in ϕ^{OX} with distance from the oxide surface. Equation 6.9 defines the conditions of anodization and properties of materials that must be met in order to initiate nanopores. Explicit expression for both sides of Equation 6.9 are derived in Appendix A. Using the expression for $\partial^{OX} \Delta^S \phi_{actual} / \partial x$ presented in Equation A.1 and the expression for $\delta^{OX} \Delta^S \phi_e / \delta x$ presented in Equation A.8, the criterion for breakdown of the planar oxide/electrolyte interface for the case of reductive dissolution of the oxide is

$$\frac{[V/\Delta]}{(d\Delta/dt)} < \frac{(z-2)}{2(z-u)F} [\Delta G_{O^{2-}}/D_{O^{2-}}] \frac{(1-y)}{y^2}$$
(6.10)

where Δ is film thickness, y is $[M^{+z}]$ at the oxide surface, $d\Delta/dt$ is the dissolution rate of the oxide, and $D_{O^{2-}}$ is the oxygen diffusivity in the oxide. The left side of the inequality represents processing parameters, e.g., electric field through the oxide (V/Δ) , and oxide dissolution rate (controlled by fluoride and hydrogen ion concentrations), while the right side refers to the oxide's surface composition. The criterion for initiation of nanopores is sketched in Figure 6.5, which makes clear the key requirements for initiation of nanoporosity: (i) y(x = 0) must be less than unity; (ii) as y(x = 0) decreases, the range of values of $(V/\Delta)/(d\Delta/dt)$ that create nanopores increases; (iii) for a given value of y(x = 0), the initiation of nanopores is favored by a small electric field in the oxide and a high value of the ratio of oxide dissolution to the diffusivity of O^{2-} in the oxide.



Figure 6.5. Criterion for the initiation of nanopores as a function of y. As y increases, smaller electric fields (V/Δ) or higher dissolution rates $(d\Delta/dt)$ are required for nanopores to be stable.

6.2.6 Chemical Dissolution of the Oxide

In the event that the oxide does not undergo electrochemical reductive dissolution, the stability of a negative perturbation in the planar interface depends on chemical dissolution of the oxide. The criterion for the breakdown of the planar interface during dissolution is developed in Appendix B

$$\Delta G_{tip} < \Delta_{planarsurface} \tag{6.11}$$

An alternative expression of Equation 6.11 is

$$\partial \Delta G / \partial x|_{oxide/electrolyteinterface} < 0$$
 (6.12)

Equations 6.11 and 6.12 define the conditions of anodization and properties of materials that must be met in order to initiate nanopores for the case in which the oxide dissolves chemically.

Note that the criteria for planar oxide instability for the case of chemical dissolution is similar to that of reductive dissolution. The breakdown criteria indicates that the planar interface will be stable, and nanoporous oxide will not develop during anodization, if $\delta ln K_D / \delta x$ equal 0, where K_D is the equilibrium constant of the oxide's chemical dissolution reaction (see Appendix B). That is, if the oxide is chemically homogeneous in the region of the oxide/electrolyte interface, the planar interface will not breakdown into a nanoporous structure. The dissolution of the oxide might continue but the interface will remain planar during dissolution. To maintain a compositional gradient in the vicinity of the oxide/electrolyte interface, in order to facilitate nanopore formation, it is necessary that the cation transport coefficient be less than unity. Thus, one requirement for the formation of nanopores during anodization is that the cation transport coefficient be less than 1.

6.2.7 Validity of the Planar Interface Instability Criterion

Substituting the values of V/Δ , $d\Delta/dt$, and y into Equation 6.10 would predict whether or not nanopores initiate according to the planar interface instability criterion (PIIC). Although the values of Δ , $d\Delta/dt$, and y are not well known for most systems, Equation 6.10 can be used to qualitatively evaluate the validity of the theory. In particular, PIIC predicts that nanopores are more likely to form if $d\Delta/dt$ is large, which is achieved by the addition of anions such as F⁻. It is well-established that nanopores will not form during anodization unless specific anions such as F⁻ are present in the electrolyte. Second, $d\Delta/dt$ predicts that nanopores are more likely to initiate if y is sufficiently less than one. The cation transport coefficients of valve metal oxides in which nanopores or nanotubes have been created are listed in Table 6.1. As required by the interface stability criterion for nanopore initiation, all of the cation transport coefficients are significantly less than unity. Finally, PIIC predicts that nanopores will form when the electric field through the oxide, V/Δ , is below a critical value. The prediction of a critical electric field cannot be verified at this time, because individual values of V and Δ at the point of nanopore initiation have not been reported.

6.3 Nanopore/Nanotube Size and Spacing

The size and spacing of nanopores and nanotubes are important parameters which govern the properties of oxide nanostructures and are established by the process of pore nucleation. This section will develop an expression for the spacing of nanopore nuclei based on the planar instability initiation criterion (PIIC). The results provide estimates of pore spacing/size that are consistent with experimentally measured values of titanium oxide. In addition, the

Metal	Cation Transport	Observation of
	Coefficient	Nanopores
Ti	0.35^{a}	Zwilling et al. [1999]
Ta	0.24^{b}	Sieber et al. [2005b]; Wei et al. [2008]
W	0.37^{b}	Mukherjee et al. [2003]
Zr	$< 0.05^{b}$	Tsuchiya et al. [2005b]
Hf	$< 0.05^{b}$	Tsuchiya and Schmuki [2005]
Nb	0.5^a	Choi et al. [2006]; Sieber et al. [2005a]
a Lohrengel	1003]	

Table 6.1. Cation Transport Coefficient of Valve Metal Oxides

^a Lohrengel [1993] ^b Pringle [1980]

analysis explains three key experimental observations from Chapter 3: (i) the simultaneous and homogeneous initiation of nanopores, (ii) the transition from disorganized to organized arrays of pores, and (iii) the increase in pore spacing/size with applied voltage.

6.3.1Qualitative Description of Spacing of Nanopores

The formation of dents in the planar interface is driven by changes in the compositions of the electrolyte and especially the oxide during the anodization process. Because the dents eventually grow into nanopores, the spacing of the dents determines nanopore spacing. This spacing can be estimated by modeling the interface by a collection of sine waves with infinitesimal amplitude and various wavelengths, λ . The driving force for perturbing the planar interface is, in part, the compositional changes in the vicinity of the oxide/electrolyte interface. Anodization adds metal ions $[M^{+z}]$ to the oxide at the metal/oxide interface and oxygen ions $[O^{2-}]$ to the oxide at the oxide/electrolyte interface. Dissolution of the oxide deposits M^{+z} and OH^{-} into the electrolyte. The combination of anodization and oxide dissolution creates an oxide surface that is depleted of M^{+z} . Because of the curved shape of the dent, growth of the dent into the oxide (Figure 6.6) requires transport parallel to the planar interface in both the oxide and electrolyte. Lateral transport is assisted by a small value of λ , which decreases the diffusion distance. However, small values of λ also increase local surface curvature and surface area. Consequently, it is expected that the wavelength of the fastest-growing perturbation will be of intermediate size and will result from a compromise between the effects of surface curvature, interfacial energy, and transport.



Figure 6.6. Breakdown of planar oxide/electrolyte interface. As the oxide dissolves, the nonplanar interface moves from right (the solid line) to left (the dashed line); the segment CA' swings outward to the line AA', and the segment CB' swings outward to the line BB'. Movement of the interface from CA' to AA' requires transport of ions in the w direction

6.3.2 Quantitative Estimates of Nanopore Spacing for the case of

Reductive Dissolution

Calculation of the wavelength of the fastest growing sinusoidal perturbation, λ_o , requires consideration of the gradients of potential and composition as well as surface curvature and surface energy. An estimate of λ_o can be obtained by borrowing from an approach used to determine the spacing between cells during solidification. [Kurtz and Fisher, 1998] This approach yields a value of the smallest wavelength capable of growing, λ_i , which is a lower limit to the value of λ_o .

 λ_i is determined by calculating the difference between the actual potential drop and the equilibrium potential drop at the tip of the dent. Specifically, if the dent is just stable, the potential drop across the oxide/electrolyte interface at the tip should be equal to the interfacial potential drop at the mouth of the dent plus the change in equilibrium potential associated with differences in the oxides composition at the dent's tip and mouth, plus the change in equilibrium potential associated with the surface curvature:

$${}^{OX}\Delta^S\phi^{tip} = {}^{OX}\Delta^S\phi^{mouth} + (\delta^{OX}\Delta^S\phi_e/\delta x)\delta + \Gamma\kappa$$
(6.13)

where δ is the length of the dent (or amplitude of the sinusoidal perturbation) and $(\delta^{OX}\Delta^S\phi_e/\delta x)\delta x$ is the change in equilibrium value of the interface potential drop resulting from a shift, δx , in the location of the interface. Γ describes the influence of curvature of the oxide-solution interface on the potential, and κ is the interface curvature.

The equalities expressed in Equation 6.13 are derived from the following descriptions of the individual terms. ${}^{OX}\Delta^S\phi^{mouth}$ is equal to the equilibrium potential, because the mouth of the dent is located at the planar interface, where the oxide is at equilibrium with the electrolyte. Starting at the location of the planar interface and creating a dent by traveling into the oxide, the equilibrium potential increases because of the increase in [M+z] with distance from the planar oxide/electrolyte interface. The actual (as opposed to the equilibrium) potential drop across the interface at the tip of a dent, ${}^{OX}\Delta^S\phi^{tip}$, also increases with distance from the planar interface because of the applied (anodization) voltage. The curvature (κ) of the sinusoidal perturbation, $x = -\delta/2 + (\delta/2) \sin(2\pi w/\lambda)$, is approximately the second derivative, $d^2x/dw^2 = -(2\pi/\lambda)^2(\delta/2) \times \sin(2\pi w/\lambda)$ evaluated at $w = \lambda/4$ (location of originally planar interface) and $3\pi/4$ (tip of dent)

$$(\lambda_i/2\pi)^2 = \frac{\Gamma}{\partial^{OX} \Delta^S \phi/\partial x - \partial^{OX} \Delta^S \phi_e/\partial x}$$
(6.14)

Perturbations with wavelengths shorter than λ_i , the minimum stable wavelength, shrink rather than grow. A more comprehensive analysis shows that perturbations with wavelengths > λ_i grow at different rates depending on the values of λ , [*Raja et al.*, 2005] while the wavelength of the fastest-growing perturbation is greater than λ_i but is still a small value in order to enhance lateral transport. Equation 6.14 indicates that λ_i depends on the composition of the oxide and electrolyte (i.e., the term $\partial^{OX} \Delta^S \phi_e / \partial x$) and on the conditions of anodization (i.e., the term $\partial^{OX} \Delta^S \phi / \partial x$). In particular, λ_i depends on the applied potential (V) as $\partial^{OX} \Delta^S \phi / \partial x \approx -V/\Delta$.

Equation 6.14 is quantitatively evaluated in Appendix C. The final result is

$$(\lambda/2\pi)^2 \approx \frac{\Gamma}{A - V/\Delta} \tag{6.15}$$

where A, a positive number, is $\{(z-2)/[2(z-u)F]\}(1/y^2)[(1-y)/x_{space-charge})]\Delta G_{O^{2-}}$ (see Equation C.4 and C.7) and is a function of the oxide composition, namely, the concentration of metal cations at the oxide surface. Equations 6.14 and 6.15 indicate that the surface region of the oxide must be depleted below the stoichiometric composition of metal cations (i.e., y must be <1; otherwise, A will be 0) in order for the dissolution of the oxide to form dents (which grow into nanopores) on the planar oxide/electrolyte interface. Thus, Equation 6.15 helps to explain why nanopores and nanotubes can form during the anodization of titanium, because the cation transport coefficient of TiO₂ is significantly less than one. Finally, Equation 6.15 indicates that the spacing of nanopores/nanotubes should increase with the anodization voltage.

6.3.3 Nanopore Spacing for the case of Chemical Dissolution

In the event that the oxide does not undergo electrochemical reductive dissolution, the stability of a negative perturbation in the planar interface depends on chemical dissolution of the oxide. The criterion of planar interface instability during chemical dissolution is presented in Equation 6.16

$$\Delta G_{tip} < \Delta G_{plane} \tag{6.16}$$

where both sides of the inequality are negative. Equation 6.16 defines the conditions that must be met to initiate dents/nanopores during anodization when the dissolution of the oxide occurs chemically rather than by electrochemical reduction. While the chemical-dissolution step does not directly depend on potential, the main external parameter is still voltage. Because ΔG_{tip} is determined by the variation of oxide composition with distance from the oxide/electrolyte interface, it is related to the condition of anodization (applied voltage). The right side of Equation 6.16 represents the intrinsic properties of the materials involved in the anodization, e.g., the composition of the electrolyte (i.e., $[H^+]$) and composition of the oxide (i.e., y).

As shown in Appendix C, the separation of dents in an anodized oxide undergoing chemical dissolution is given by

$$(\lambda_i/2\pi)^2 = \frac{\Gamma}{kT(\partial\Delta G_D/\partial x)}$$
(6.17)

The discussion in Appendix C indicates that in the absence of compositional gradients in the oxide and electrolyte, $\partial \Delta G_D / \partial x = 0$, so that $\lambda_i = \infty$, and the planar interface is stable. As was the case for electrochemical reductive dissolution, the formation of dents that grow into pores requires depletion of metal cations in the oxide near the electrolyte, which again can happen if the cation transport coefficient is significantly less than unity.

Evaluation of the individual terms that contribute to $\partial \Delta G_D / \partial x$ indicate that $\partial \Delta G_D / \partial x$ is a function of the anodization voltage, and thus λ_i increases with applied voltage but in a manner that depends on the exact voltage dependency of y(x = 0). Based on the assumption that y(x = 0) decreases as the anodization voltage increases, and that the voltage dependency of y(x = 0) is given by $1/(\alpha V + 1)$ (Appendix C), the spacing of nanopores/nanotubes for the case of chemical dissolution is given by:

$$\lambda_i / = \frac{\Gamma}{(\partial y / \partial x)(B - 1 - \alpha V)} \tag{6.18}$$

This expression is identical in form to that derived for the case of electrochemical reductive dissolution. That is, the breakdown of the interface requires a critical minimum value of y(x=0) and the spacing of dents (nanopores) to increase as the voltage increases.

In brief, chemical dissolution leads to breakdown of the planar oxide/electrolyte interface only if the metal cation transport number is significantly less than one, which allows for $\lambda_i > 0$. A homogeneous oxide can be chemically dissolved, but the dissolution does not result in breakdown of the planar interface. The minimum wavelength of the sinusoidal perturbation that describes the broken down interface increases with anodization voltage.

6.3.4 Comparison of Predicted and Measured Influence of Voltage

on Nanopore/Nanotube Spacing

After making the appropriate substitutions (details provided in Appendix C) into Equation 6.14 the final expression for λ_i is

$$(\lambda_i/2\pi)^2 = \frac{1.66 \times 10^{-8} V cm}{(1/2F)[(1/x_{space-charge})(\Delta G_{O_{2-}})((1-y)/y^2) - V/\Delta]}$$
(6.19)

Estimates of λ_i require values of $x_{space-charge}$, y, V/Δ , and $\Delta G_{O^{2-}}$. The values of these parameters for the case of Ti anodization have not been reported in studies to date. As discussed in Appendix C, 10 nm is a reasonable value of $x_{space-charge}$. The influence of y, V/Δ , and $\Delta G_{O^{2-}}$ on λ_i is graphically illustrated in Figure 6.7, which shows the plots of λ_i vs V/Δ , the average electric field through the oxide. Each figure corresponds to a particular value of $\Delta G_{O^{2-}}$, (27 eV and 6.75 eV, see discussion in Appendix C) and in each plot there is a family of curves, with each curve representing a value of y(x = 0). The results are strongly dependent on the y(x = 0) value.

The next step is to compare the predictions of Equation 6.19 and Figure 6.7 with experimental results. First, experimental measurements of λ_i are not readily available but a number of measurements have been made for λ_o . Figure 6.8 compares the calculated values of λ_i to measured values of λ_o in both the organized and disorganized layers. The results indicate that λ_i does represent a lower limit to the values of λ_o , as required by our model, and both values are within the nanometer range. Second, as already mentioned, values of $x_{space-charge}$, y, and V/Δ have not been measured in studies to date. However, estimates $x_{space-charge}$, y, and V/Δ can be extracted from the data of Taveira et al. [2005]. The authors report that pores first appear during anodization at 20 V when the film thickness is in the range of 40-50 nm. From X-ray photoelectron spectroscopy (XPS) measurements, the width of the space-charge region is assumed to be approximately 10 nm, and the value of y at the surface of the oxide is approximately 0.5 (the authors suggest $Ti(OH)_4$ forms on the surface and TiO_2 in the bulk of the oxide). Substituting these values into the expression for λ_i and setting $\Delta G_{O^{2-}} = 27$ eV yields a value of $\lambda_i = 1.8$ nm. As can be seen in Figure ??, the value calculated for λ_i is sensitive to the value of y. For example, using y = 0.6yields $\lambda_i = 2.6$ nm, and for y = 0.77, $\lambda_i = 17$ nm. The value of λ_o obtained by Taveira et al. [2005] is approximately 100 nm, while as reported in Chapter 3, titanium foil anodized under similar conditions have yielded $\lambda_o = 60$ nm. Both measurements of λ_o are consistent with the calculations of λ_i , given the uncertainty in estimated values. It should be noted that the calculated values of λ_i were obtained without the benefit of adjusting any parameters in Equation 6.19, so as to fit the calculations to measurement of λ_o at a particular value of V.

As shown in the plots presented in Figure 6.7, λ_i increases with V/Δ . This result is consistent with the experimentally observed increase in λ_o with V. As previously mentioned, the present analysis does not provide an expression for λ_o . Nevertheless, the experimentally observed linear increase in λ_o vs V (Figure 3.3) is consistent with the slopes of the approximately linear regions of λ_i vs V/Δ in Figure 6.7.



Figure 6.7. Influence of electric field strength, $|V/\Delta|$, on the minimum spacing of dents in the oxide/electrolyte interface: (a) the value of $\Delta G_{O^{2-}}$ is 27 eV, the estimated upper limit of free energy of formation and (b) $\Delta G_{O^{2-}}$ is 6.75 eV. Each curve in the figures corresponds to a particular value of y(x = 0).



Figure 6.8. Comparison of calculated λ_i vs experimentally observed λ_o . [*Raja et al.*, 2005; *Macak et al.*, 2008; *Bauer et al.*, 2006] The range of λ_i was calculated using $\Gamma = 1.66 \times 10^{-10} Vm$, $x_{space-charge} = 10$ nm, $\Delta G_{O^{2-}} = 27$ eV, and $V/\Delta = 5 \times 10^8$ V/m (20 V/40 nm), with y = 0.05 to 0.75.

In addition, Equation 6.19 indicates that y(x = 0) must be less than a critical value, y^* , in order for λ_i to have a real value (i.e., in order for the numerator in Equation 6.19 to be positive). Again, using the values of V/Δ and $x_{space-charge}$ from the study of *Taveira* et al. [2005], and setting $\Delta G_{O^{2-}} = 27$ eV, Equation 6.19 indicates that y^* , the maximum value of y, is 0.78, which is consistent with the measured value of y = 0.5 (approximate). The requirement that y must be less than a critical value y^* (achieved by a cation transport coefficient that is significantly less than one) is also consistent with the low measured values of the cation transport coefficients of titanium, tungsten, zirconium, and niobium, all of which have exhibited nanoporous oxides as a result of anodization in appropriate electrolytes. (Table 6.1 Thus, there is good qualitative agreement between the plots presented in Figure 6.7 and experimental observations.

Finally, Equation 6.19 and the results presented in Figure 6.7 provide several additional predictions that cannot be verified at this time due to a lack of experimental measurements. In particular, the results indicate that for a given value of y, the planar interface will be stable above a critical value of V/Δ and that below the critical value, nanopores can form.

Second, for a given value of y, λ_i is approximately linearly dependent on V/Δ over a fairly wide range of V/Δ , and above this region λ_i increases sharply with V/Δ .

6.3.5 Transition from Disordered to Ordered Arrays of Dents

The proposed mechanism of nanopore initiation also explains the transition from a disorganized array to an organized array, which was observed experimentally (Figure 3.6, Figure 3.13, and Figure 3.14) and is evident in scanning electron micrographs presented in a number of other papers. [*Raja et al.*, 2005; *Taveira et al.*, 2005; *Lim and Choi*, 2007; *Gong et al.*, 2001; *Mora et al.*, 2003] Specifically, the anodized surface is first covered with a disorganized nanoporous oxide. In time, an organized nanoporous film is formed underneath the disorganized layer.

As described above, and demonstrated in Figure 6.9, breakdown of the planarity of the oxide/electrolyte surface initially occurs by the formation of a number of sinusoidal perturbations of different wavelengths. Each perturbation grows in amplitude at a rate dependent on its wavelength. Because of the wavelength dependency of the perturbations' growth rates, the surface initially consists of a disorganized array of nanopores (Figure 6.9ii). Eventually, the array of nanopores is organized with a spacing equivalent to the wavelength of the fastest-growing sinusoidal perturbation (Figure 6.9iii).

6.4 General Comments on Planar Interface Instability

Criterion

Both solidification cells/dendrites and nanopores are a consequence of compositionalinduced instabilities in the planar liquid/solid interfaces. According to the planar interface instability model, nanopore/nanotube spacing is a consequence of compositional and voltage gradients induced by the anodization process, which breaks down the planar interface. Similarly, the formation of cells and dendrites during the freezing of a liquid alloy is a consequence of compositional and temperature gradients induced by the solidification process. [Kurtz and Fisher, 1998; Tiller, 1991] However, there are several significant differences between the formation of solidification cells and the formation of nanopores. First, solidification cells grow in the same direction as the movement of the liquid/solid interface. Nanopores, however, grow into the oxide from a planar oxide/electrolyte interface that is either essentially stagnant (because the anodized oxide is growing primarily at the metal/oxide interface) or growing in the opposite direction of the nanopores (if oxide growth occurs at oxide/electrolyte interfaces). Second, in the formation of solidification cells, transport in the solid is of little consequence. In the formation of nanopores, ion transport through the solid is a significant factor in the



Figure 6.9. Evolution of shapes of oxide/electrolyte and oxide/metal interfaces: (i) planar oxide/electrolyte interface, (ii) breakdown of planar oxide/ electrolyte interface and formation of sinusoidal perturbation of different wavelengths, and (iii) continuation of breakdown of planar oxide/electrolyte with development of nanopores. The spacing of the pores corresponds to the wavelength of the fastest growing sinusoidal perturbation. High electric field through the oxide at the locations of pores increases growth of oxide into the metal and creates a scalloped metal/oxide interface.

breakdown of the planar interface. Third, the spacing of cells is largely controlled by the temperature gradient, while the spacing of nanopores is largely controlled by the voltage gradient. Much larger voltage gradients are possible during anodization than temperature gradients during solidification. As a result, cell spacings are typically on the order of 1-100 μ m, while nanopore spacings are on the order of 25-300 nm. [Macak et al., 2007; Tsuchiya et al., 2005a; Paulose et al., 2006]

Chapter 7

Concluding Remarks

Titania nanotubes are among a group of highly exciting material systems as they can be employed in a wide range of applications. Arrays of nanotubes have been used as electrodes in solar cell devices and batteries, as well as highly effective supporting matrix for carbon in fuel cells. Other potential applications include gas sensors, water photoelectrolysis, and photocatalyst devices. Understanding the formation mechanism, as well as the effects of synthesis conditions on the material's structure and properties, are among the key steps to successfully employing titania nanotubes in devices. The last few chapters examined the fundamental growth and structure properties of electrochemically grown titania nanotubes, as well as offered a proposed theory for the nucleation and growth of these structures. The main points from this work are highlighted below.

7.1 Growth

Electrochemically synthesized titania nanotubes offer a high degree of control over their structure and morphology via manipulation of the synthesis parameters. The highly-ordered and vertically oriented titania nanotubes are formed via anodization of a Ti substrate in a fluoride containing electrolyte. The nanotubes have an open top and closed bottom, and a narrow distribution of tube diameter, spacing and lengths. The anodization voltage can be tuned to obtained nanotubes with desired diameter values, while the length of the tubes can be controlled with the synthesis time and electrolyte composition. For example, in a growth solution composed of 0.5 wt% NH₄F in ethylene glycol, anodization of Ti at 20 V for 1 hour will yield nanotubes that are approximately 40 nm in diameter and 1.5 to 2 microns in length. Experimental results indicate that the relationship between the anodization voltage and diameter is approximately linear, while the anodization time is logarithmically related to the nanotube length. The growth rate decreases with time, as the length of the nanotubes increases.

Other factors that can affect nanotube formation and growth include the electrolyte chemistry. Specifically, the type of solvent, the electrolyte pH, and the active anions in solution can all affect the growth process. As discussed, acidic pH can limit the length of the nanotubes while solutions with more neutral pH will allow nanotubes to grow to hundreds of microns long. Viscous solvents, such as ethylene glycol, allow for the formation of smoother wall nanotubes vs aqueous solvents. The active anions in solution however has the biggest effect on nanotube formation.

Organized nanotubes appear to only form in fluoride containing electrolyte. While anodization in electrolytes with Cl⁻ and Br⁻ as the active anions also resulted in nanotube formation, the tubes grow from pits in the surface oxide and do not uniformly cover the substrate. Although tubes grown in Br⁻ and Cl⁻ based electrolyte do not have the self-organized structure of those seen in F⁻ solutions, the growth rates are much faster, achieving tens of microns in length in 60 s. Other interesting differences between these tubes and those formed in F^- solutions include: (1) the tube's diameter, on average about 15 nm, is much smaller than their counterpart for a given applied potential. (2) The anodization potential does not affect the diameter of the tubes. Instead, higher anodization potential leads to the initiation of more pits, within which the nanotubes form. (3) Viscous solvents, such as ethylene glycol (EG) and glycerol do not enhance the growth of these tubes, but in fact dampen it. Synthesis done in EG or glycerol solutions leads to tubes that are only 3 or 4 nm long, regardless of synthesis time. (4) The presence of water on the other hand greatly increases the growth rate of the tubes. However, in pure water, the nanostructure that form is more fiber-like than tube-like. While these nanotubes are not organized, they offer some obvious advantages. Besides their fast growth rate, nanotubes formed in these electrolytes can be synthesized without using hazardous chemicals. That is, these long tubes can be produced quickly and in a safe manner. In addition, their high aspect ratio may make them ideal for many applications such as photocatalysis and chemical sensing.

The observed differences between nanotubes grown in Cl^- and Br^- vs. those formed in F^- solutions lead to the conclusion that the growth mechanisms are different in the two types of electrolytes. A focused-ion-beam (FIB) cross-section of samples anodized in Cl^- and Br^- electrolytes confirm that the nanotubes grow from pits that had formed on the surface oxide and thus tend to form clusters. On the other hand, nanotubes formed in F^- electrolytes do not exhibit this characteristic.

Experiments looking at the time progression of nanotube formation in F^- based electrolytes indicate that the tube formation process starts with a porous top layer. The porous layer appears simultaneously and homogeneously over the entire surface of the substrate very early on in the process (after 30 seconds of anodization). The pores coalesce and expand in both diameter and length with time. Underneath the initial porous layer, the tubular layer develops and is eventually revealed when the top porous layer dissolves. These observations are not consistent with a pitting mechanism but with an interface breakdown process. In fact, experimental results show that in samples with pre-formed pits on the surface, the pits

do not elongate with anodization, but experiences the same nucleation steps as those without pits on the surface.

Further studies indicate that pore initiation and pore growth are distinct steps. Experiments involving 2-step anodization processes reveal that growth of the nanotubes during metal anodization is enabled by very specific electrolyte and oxide chemistries inside the tubes. If the anodization process is interrupted for a long period of time so that the electrolyte inside the tubes has time to equilibrate itself with the bulk solution, nanotube growth will not continue. Instead a re-nucleation process will occur and a second layer of nanotubes will appear beneath the top layer. On the other hand, if the interruption is short (30 seconds or less), so that the unique electrolyte composition near the oxide/electrolyte interface is maintained, nanotube growth will continue and the sample will have one uniform nanotube array.

As for the case of nucleation, the process appear to only occur in "fresh" oxide, i.e. oxide currently being formed by anodization. Synthesis runs using substrates with pre-formed oxides on the surface results in the "dead" surface oxide being shed via chemical etching (but not one that produces homogenous pores). The pore nucleation steps, and subsequent nanotube growth, appear to only occur in the "fresh" oxide growing underneath. The need for "fresh" oxide is consistent with the requirement for particular compositions of the interfacial electrolyte and interfacial oxide that develop during the anodization process.

In summary, experimental results reveal that the unique electrolyte composition near the oxide/electrolyte interface is vital for the continuation of tube growth. This composition likely allows for fast dissolution of the oxide at the tube bottom and enable further oxide formation and tube elongation. The nucleation step on the other hand is a dynamic process that involves oxide currently being formed via anodization, and requires particular compositions in the electrolyte and oxide near the interface.

7.2 Structure and Composition

The crystal structure, morphology, and composition of electrochemically grown titania nanotubes were investigated to better understand the effect of processing parameters and determine the applicability of these nanostructures in devices.

The structure and fine morphology of titania nanotubes were examined in detail, via cross-sectional and high-resolution transmission electron microscopy (TEM). The microscopy images reveal that the tubes have highly oriented growth direction in relation to the metal substrate, always growing perpendicular to the substrate. Cross-sectional images also confirm the existence of a barrier-oxide layer that exists between the nanotubes and the metal substrate, which is sculpted at both interfaces. The sculpting of the interfaces gives an indication of where the pore/tube initiation occurs, at the metal/oxide interface or the oxide/electrolyte interface.

The crystal structure of the nanotubes were determined primarily by micro x-ray diffrac-

tion (XRD) analysis. The results indicate that the nanotubes, in their as-grown state, are amorphous. With a heat-treatment temperature of 450°C and above, the amorphous oxide crystallizes into a polycrystalline mixture of anatase and rutile, both polymorphs of titania. The higher the heat treatment temperature, the higher the rutile percentage, and the lower the sample porosity. The nanotube morphology is maintained at temperatures of 450°C and below, while above this temperature, a breakdown of the tube morphology occurs through high temperature sintering effects.

Close examination of the XRD data reveals that with a 450°C heat-treatment temperature, the nanotube oxide is primarily anatase, with a small amount of rutile ($\approx 10\%$), while the barrier layer oxide is entirely rutile in structure. The resulting difference in crystal structure of the two oxide layers is attributed in part to differences in oxide morphology. While rutile is the thermodynamically stable phase of titania, and anatase is metastable, it has been found that at small crystallite sizes in the nanometer range, anatase is actually the more stable phase due to its lower surface energy. The thickness of the nanotube wall (between 5 and 20 nm) limits the size of crystals that can form in the nanotube layer and suppresses the anatase to rutile transformation. The critical nucleus size required for the transformation is usually not achieved in the tube wall. The crystals in the barrier layer oxide however do not experience any lateral constraints to their size and therefore can more easily transform to rutile.

Although XRD results indicate that the as-grown nanotube oxide is entirely amorphous, high-resolution TEM work indicates that the nanotube oxide is actually semi-crystalline in nature. In particular, nano-crystallites are embedded within the amorphous matrix that make up the barrier oxide. These crystallites are likely anatase, but their size was too small to allow definitive identification. Cross-sectional TEM was also used to investigate the crystal structure of the nanotube and barrier layer after heat-treatment. Results confirm the XRD data, that the nanotube oxide is composed of a mixture of anatase and rutile, while only rutile crystals can be found in the barrier layer. The high-resolution TEM images reveal that all the rutile crystals examined are oriented in the same direction, indicating that the barrier layer is highly textured. The crystals also appear strained as their spot patterns are distorted. These results suggests that crystallization of the barrier layer oxide is likely influenced by the titanium substrate. Because titanium's htp structure has very similar lattice parameters to rutile (although not perfectly matching), rutile crystals probably nucleate near the oxide/metal surface and adopt an orientation that allows for minimum mismatch between the two structures. The slight mismatch in their lattice parameters, although small, produces a small strain field in the crystals.

The compositions of the nanotube and barrier layer oxides were probed using energy dispersive spectroscopy (EDS) and electron energy loss spectroscopy (EELS). In both the as-grown and heat-treated nanotube samples, there are marked differences in the composition of the nanotube and the barrier layer oxides. EDS line scans analysis shows that the composition of the nanotube oxide is uniform through the length of the tube, while the composition of the barrier layer oxide varies through its thickness. The barrier layer oxide shows higher oxygen concentration near the electrolyte/oxide interface, and higher titanium concentration near the oxide/metal interface. Another notable result is the incorporation of

 F^- anions into the oxide structure, where the F^- signal is the highest in the nanotube oxide and become non-existent in the metal substrate. EELS analysis also confirms these results. The EELS elemental maps of titanium, oxygen and fluoride ions show a difference in oxygen concentration in the barrier layer vs the nanotube oxide. The difference in the composition of the nanotube oxide and barrier layer oxide indicate that the two layers possibly represent different stages of the oxide during nanotube growth and formation.

As mentioned in the introduction, titania nanotubes have promise as electrodes in a series of solar cell devices, including dye sensitized solar cells. However, the presence of a polycrystalline material suggests that these nanotube structures, in their present state, might not yield significant advantages over the nanoporous titania used in dye sensitized solar cells. One of the advantages of the tube, or wire, structure is that it offers a direct transport path for traveling electron, as opposed to the tortuous path typically seen in titania nanoparticles. [Law et al., 2005; Mor et al., 2006] However, a polycrystalline tubular structure that is electrically connect in the lateral direction to other tubes offers the same tortuous paths for electrons. In order to make these materials more ideal for DSSC applications, the nanotubes should be electrically insulated from their neighbors, to impede lateral transport, as well as single crystalline, so that grain boundaries cannot act as recombination sites for photon generated electron-hole pairs. Such a structure can offer increased efficiency by speeding up transport time and reducing recombination loses. It has been documented that the creation of a smooth, filament-free nanotube structure can be achieved with more viscous solvents such as glycerol. [Macak and Schmuki, 2006; Yin et al., 2007] The challenge then is to generate a nanotube structure that is single crystalline.

Heat-treatment of the nanotubes is needed in order to obtain the crystalline structure useful in devices. A nanotube array that is single-crystalline, whether anatase or rutile, is ideal. Because previous work shows that an oxide layer with an entirely rutile crystal structure loses its tubular morphology [Lin et al., 2003], focus falls on generating nanotubes that are purely anatase and single crystalline. This effort is complicated by the fact anatase is typically only stable at small crystallite sizes. Beyond a certain crystal size, it will thermo-dynamically favor the formation of rutile. Unless engineering processes can be developed to entirely inhibit this transformation, the generation of a single-crystalline array of electrochemically synthesized titania nanotubes will be out of reach. The work by Shannon and Pask [1965] and Hishita et al. [1983] shows that there is promise for generating large arrays of single-crystalline anatase, but further studies on the crystallization kinetics of titania nanotubes need to be completed.

7.3 Nanotube Formation and Initiation Model

The mechanism responsible for the formation of organized arrays of nanotube can be considered to be composed of two distinct steps, the initiation of the pores and growth/elongation of the pores. While many models exist to describe the growth of the pores/tubes, the initiation stage is usually only ascribed to pitting at unspecified defect sites. Experimental results from this work indicate that that the pitting model is not sufficient to describe the formation of nanotubes. Instead, a planar instability initiation criterion (PIIC) can be used to describe the initiation mechanism. The mechanism proposes that initiation occurs via brake down of the planar interface, induced by compositional gradients in the oxide and electrolyte that result from the anodization process.

Arrays of nanopores and nanotubes are initiated by the breakdown of the planar oxide/electrolyte interface. Depressions or dents form across the entire surface of the oxide as a consequence of compositional changes in the electrolyte and in the oxide that destabilize the planar surface. The dents, or surface perturbations, are modeled by a series of sine waves whose growth rates are a function of their wavelengths. In particular, for $\lambda < \lambda_i$ the sine wave shrinks rather than grows, while for $\lambda > \lambda_i$, the growth rate is a function of λ . For $\lambda = \lambda_o$, which is slightly greater than λ_i , the growth rate is a maximum and is responsible for the transition from a disorganized array to an organized array of nanopores. The model, in agreement with experimental results, predicts that λ_i increases with the applied voltage, V, and is approximately linearly proportional to V.

Arrays of dents, which lead to nanopores and nanotubes, should form in oxides that reductively or chemically dissolve and whose dissolution rate is accelerated by electrolyte species that complex metal cations or catalyze the oxides chemical dissolution. The proposed criterion for nanopore initiation is consistent with the following experimental observations. (i) Nanopores initiate simultaneously across the entire surface, and (ii) the initiation requires the presence in the electrolyte of species that complex metal cations or catalyze oxide dissolution. (iii) The initiation also requires a metal cation transport coefficient through the oxide that is significantly less than unity. (iv) The nanopores transition from an initially disorganized array to an organized array. (v) In addition, the spacings of nanopores/nanotubes that ultimately form are in excess of the predicted minimum value, and (vi) these diameters/spacings increase as the applied voltage increases.

The validity of the interface breakdown mechanism is supported by observations made primarily by researchers regarding the formation of nanopores and nanotubes in titanium oxide. Although proposed for the specific case of anodization of titanium, the mechanism could also be applicable to other valve metals. However, the formation of nanoporous oxides is a complicated process, and there is no current evidence of the widespread applicability of this mechanism. Further studies is need to examine whether PIIC can be used to describe nanopore/nanotube formation in other valve metal oxides.

Appendix A

Compositional and Potential

Gradients in the Oxide

A.1 Value of $\partial^{OX} \Delta^S \phi / \partial x$

The term $\partial^{OX} \Delta^S \phi / \partial x$ is set equal to the ratio of the anodization voltage (V) to the thickness of the anodized oxide (Δ)

$$\partial^{OX} \Delta^S \phi_{actual} / \partial x = -V/D \tag{A.1}$$

The proper value of V/Δ to insert into Equation A.1 is the value at which breakdown of the interface's planarity begins. During anodization, Δ increases with time. The voltage across the film also changes with time but in a manner depending on whether the anodization is performed galvanostatically or potentiostatically. In the former case, the anodization voltage increases with time. In the latter case, the voltage across the film is constant for most of the anodization. For both cases, the ratio of V/Δ is limited by the dielectric breakdown of the film. The breakdown voltage of TiO₂ is in the range of $10^7 - 10^9$ V/m. *Taveira et al.* [2005] report that with an applied voltage of 20 V, nanopores initiated when the thickness of the anodized film of titanium dioxide was 40-50 nm. Accordingly, for a number of calculations we have approximated the value of V/Δ to be 20 V/40 nm.

A.2 Value of $\partial^{OX} \Delta^S \phi_e / \partial x$

The electrochemical reduction of anodized titanium dioxide in an electrolyte containing F^- is presented in Equation 6.7 and reproduced here

$$Ti_y O_{z/2} + \frac{yz}{2}H^+ + yuF^- + y(z-u)e^- \to y(TiF_u)_{aq} + \frac{yz}{2}OH^- + \frac{z(1-y)}{2}O_{OX}^{2-}$$
(A.2)

 Ti_yO_2 represents the surface composition of anodized TiO₂, where y < 1, and indicates the titanium depletion of the oxides surface. The general nature of the reduction reaction is reflected by the unspecified oxidation state, u, of the reduced titanium. Titanium cations in TiO₂ exhibit a relatively large oxidation number of 4. A number of values of u < 4 are possible, as suggested by the existence of stoichiometric oxides such as Ti₂O₃, Ti₃O₂, and TiO, as well as the large number of Magneli phases with compositions between TiO₂ and Ti₂O₃. [Wahlbeck and Giles, 1966; Waldner and Eriksson, 1999].

The Gibbs free-energy change, ΔG , of the electrochemical reduction of Ti_yO₂ is given by:

$$\Delta G = y \Delta G_{TiF_u} + \frac{yz}{2} \Delta G_{OH^-} + \frac{z(1-y)}{2} \Delta G_{O^{2-}} - yu \Delta G_{F^-} - \frac{yz}{2} \Delta G_{H^+} - \Delta G_{Ti_yO_{z/2}}$$
(A.3)

The equilibrium potential for the reductive dissolution is

$${}^{OX}\Delta^{S}\phi_{e} = -\frac{1}{y(z-u)F} \{ y\Delta G_{TiF_{u}} + \frac{yz}{2} \Delta G_{OH^{-}} - yu\Delta G_{F^{-}} - \frac{yz}{2} \Delta G_{H^{+}} \} - \frac{1}{y(z-u)F} \{ \frac{z(1-y)}{2} \Delta G_{O_{2^{-}}} - \Delta G_{Ti_{y}O_{z/2}} \}$$
(A.4)

The right side is subdivided into two bracketed terms. The first contains free energies of species in the electrolyte, while the second contains the free energies of species in the oxide. Expressing the free energies of the aqueous species in terms of their activities gives the following expression for the equilibrium potential

$${}^{OX}\Delta^{S}\phi_{e} = \{{}^{OX}\Delta^{S}\phi_{e}^{O} - (\frac{RT}{y(z-u)F})(y\ln[(TiF_{u})_{aq}] + \frac{yz}{2}\ln K_{W} - (yz)\ln[H^{+}] - (yu)\ln[F])\} - \{\frac{1}{y(z-u)F}(\frac{z(1-y)}{2}\Delta G_{O_{2-}} - \Delta G_{Ti_{y}O_{z/2}})\}$$
(A.5)

The change in ${}^{OX}\Delta^S\phi_e$ due to a shift of δx in the location of the oxide/electrolyte interface is given by

$$\delta({}^{OX}\Delta^{S}\phi_{e}) \approx [\partial({}^{OX}\Delta^{S}\phi_{e})/\partial x]\delta x \tag{A.6}$$

Therefore

$$\delta({}^{OX}\Delta^{S}\phi_{e}) \approx [\partial/\partial x \{ -(\frac{RT}{y(z-u)F})(y\ln[(TiF_{u})_{aq}] + \frac{yz}{2}\ln K_{W} - (yz)\ln[H^{+}] - (yu)\ln[F]) \} - \partial/\partial x \{ \frac{1}{y(z-u)F}(\frac{z(1-y)}{2}\Delta G_{O^{2-}} - \Delta G_{Ti_{y}O_{z/2}}) \}]\delta x$$
(A.7)

The compositional gradients in the electrolyte $(\partial/\partial x)$ of the terms within the first set of curly brackets $\{\}$) are assumed, as a first approximation, to have a negligible effect on the gradient of the equilibrium poential. [*Bhargava et al.*, 2009] Consequently,

$$\delta(^{OX}\Delta^S\phi_e) \approx -\partial/\partial x \{ \frac{1}{y(z-u)F} (\frac{z(1-y)}{2} \Delta G_{O^{2-}} - \Delta G_{Ti_yO_{z/2}}) \} \delta x$$
(A.8)

Developing an expression for $\Delta G_{Ti_yO_{z/2}}$ as a function of y requires a thermodynamic model of Ti_yO_{z/2}, which, in turn, requires knowledge of the atomic structure of Ti_yO_{z/2}. At this time, there is no information available in the literature regarding the atomic structure of the surface of anodized titanium oxide. Anodized TiO₂ is known to be amorphous, but the atomic structure of Ti_yO_{z/2} is not yet known for small values of y. For values of y close to unity, the structure of Ti_yO_{z/2} can be thought of as TiO₂ plus point defects. However, the point-defect model is not appropriate for the small values of y that exist at the surface of TiO₂ during anodization. [Raja et al., 2005] Instead, an expression is developed for $\Delta G_{Ti_yO_{z/2}}$, based on the assumption that enthalpic effects dominate the distribution of Ti⁺⁴. The thermodynamic stability of intermetallic compounds, such as TiO₂, is largely a consequence of the low energy of TiO bonds, so that the enthalpic contribution to free energy outweighs the entropic contribution.

For guidance on the structure of $\text{Ti}_y O_{z/2}$ that is dominated by enthalpy, the structure of off-stoichiometric $\text{Ti}O_{2-x}$ is consulted. This structure is known to be dictated by enthalpic effects and consists of regions of amorphous $\text{Ti}O_2$ and titanium ion interstitials. [Anderson, 1984] As a consequence, one possible structure of $\text{Ti}_y O_{z/2}$ consists of domains of amorphous $\text{Ti}O_2$ embedded in an amorphous array of oxygen ions. Were $\text{Ti}_y O_{z/2}$ dominated by entropic effects, its structure would consist of a random distribution of Ti^{+4} in an amorphous arrangement of oxygen ions, which represents a second possible structure of $\text{Ti}_y O_{z/2}$. Thermodynamic models with larger entropic contributions were also considered; however, they did not result in criteria for breakdown of the planar oxide/electrolyte interface that were considerably different from the criterion based on the enthalpic model of $\Delta G_{Ti_yO_{z/2}}$. As a consequence, the enthalpic model was used to derive an expression for $\Delta G_{Ti_yO_{z/2}}$.

A.3 Expression for $\Delta G_{Ti_yO_{z/2}}$ with $Ti_yO_{z/2}$'s Structure

Controlled by Enthalpy

The value of y increases from its minimum value at the oxide/electrolyte interface to y = 1at the edge of the oxide's space-charge region. Thus, $\Delta G_{Ti_yO_{z/2}}$ needs to be expressed as a function of distance from the oxide/electrolyte interface. Accordingly, $\Delta G_{Ti_yO_{z/2}}$ is defined as the free energy of formation of $\text{Ti}_yO_{z/2}$ at a distance x from the oxide surface, where y at x corresponds to the ratio of the concentration of Ti^{+4} at x relative to the concentration of Ti^{+4} if the composition at x were TiO₂. For the enthalpic model, the free energy of $\text{Ti}_y O_{z/2}$, $\Delta G_{Ti_y O_{z/2}}$, is given by

$$\Delta G_{Ti_y O_{z/2}} = A_{TiO_2} \Delta G_{TiO_2} + (1 - A_{TiO_2}) \Delta G_{O^{2-}} + A_1 \sigma_1 \tag{A.9}$$

where A_{TiO_2} is the area fraction of the plane of $\text{Ti}_y \text{O}_2$ (at a distance x from the oxide surface) that is composed of domains of amorphous TiO_2 . $(1 - A_{TiO_2})$ is the area fraction of the plane of $\text{Ti}_y \text{O}_2$ that is covered by the amorphous array of oxygen ions not associated with Ti^{+4} . A_1 is the total interfacial area between the domains of TiO_2 and the array of oxygen anions.

For a given value of y, $\operatorname{Ti}_y O_{z/2}$ can exhibit a number of structures, depending on the sizes and numbers of the domains of TiO₂. It is assumed that the interfacial energy between the domains and the array of oxygen ions, σ_I , is negligible for simplification purposes. The ratio of the volume free-energy change to the surface free-energy change associated with a circular disk of amorphous oxygen ions of radius r and height h immersed in TiO₂ is given by $\Delta G_{O^{2-}} = \pi r^2 h/((\sigma_1)(2\pi rh + 2\pi r^2)))$. For arithmetic simplicity, it is assumed that r = h so that the ratio is $\Delta G_{O^{2-}} = r/(4\sigma_1)$. Using the values $\Delta G_{O^{2-}} = 27$ eV (= 25.9 ×10¹2 ergs/mole), $\sigma_1 = 1000$ ergs/cm², and a molar oxide volume of 20 cc, the ratio becomes 6.5×10^8 cm⁻¹ r. Thus, as long as the oxygen-ion regions are larger than 20 nm, which is reasonable for small values of y(x = 0), the ratio of the volume energy to the surface energy is >130, and it is a good approximation to neglect the surface-energy term in Equation A.8.

The free energy of $\text{Ti}_y O_2$ is then a function of the free energies of amorphous $\text{Ti}O_2$, ΔG_{TiO_2} , and the array of oxygen ions, $\Delta G_{O^{2-}}$.

$$\Delta G_{Ti_y O_{z/2}} = A_{TiO_2} \Delta G_{TiO_2} + (1 - A_{TiO_2}) \Delta G_{O^{2-}}$$
(A.10)

 A_{TiO_2} is set equal to y (e.g. for y=1, $A_{TiO_2}=1$, and for y=0, $A_{TiO_2}=0$)

$$\Delta G_{Ti_y O_{z/2}} = y \Delta G_{TiO_2} + (1 - y \Delta G_{O^{2-}})$$
(A.11)

Substituting into the expression for $\delta(^{OX}\Delta^S\phi_e)$ gives

$$\delta(^{OX}\Delta^S\phi_e) \approx -\partial/\partial x \{\frac{1}{y(z-u)F} (\frac{z(1-y)}{2}\Delta G_{O^{2-}} - \Delta G_{Ti_yO_2} - (1-y)\Delta G_{O^{2-}})\}\delta x \quad (A.12)$$

$$\delta({}^{OX}\Delta^S\phi_e) \approx -\partial/\partial x \{\frac{1}{y(z-u)F} (\frac{(z-2)}{2}(1-y)\Delta G_{O^{2-}} - y\Delta G_{TiO_2})\}\delta x$$
(A.13)

Because ΔG_{TiO_2} is a constant, $\partial \Delta G_{TiO_2}/\partial x = 0$, and the expression is further simplified to

$$\delta({}^{OX}\Delta^{S}\phi_{e})/\delta x = (\frac{z-2}{2(z-u)F})(\frac{1}{y^{2}})(\frac{dy}{dx})(\Delta G_{O^{2-}})$$
(A.14)

Note that $\delta({}^{OX}\Delta^{S}\phi_{e})/\delta x$ is <0 as dy/dx is <0 and $\Delta G_{O^{2-}}$ = is >0. An upper limit of $\Delta G_{O^{2-}} = 27$ eV has been calculated.[Bhargava et al., 2009]

The influence of processing conditions on the initiation of nanopores is expressed by substituting for the expression of dy/dx. Referring to Equation A.2, the electrochemical

reductive dissolution of $\text{Ti}_y O_2$ generates $(yz/2)\text{OH}^-$ and $(z/2)(1-y)(\text{O}^{2-})_{OX}$. At steady state, the amount of $(\text{O}^{2-})_{OX}$ generated on the oxides surface must equal the flux of oxygen ions into the oxide

$$(d\Delta/dt[O^{2-}]_{oxide-suface}) = D_{O^{2-}}\partial[O^{2-}]_{ox}/\partial x$$
(A.15)

where $d\Delta/dt$ is the oxide dissolution rate, $D_{O^{2-}}$ is the diffusivity of O^{2-} in the oxide, and $[O^{2-}]_{ox} = 1 - y$. Substituting $[O^{2-}]_{ox} = 1 - y$ into Equation A.15 and solving for dy/dx gives

$$dy/dx = (d\Delta/dt)(1-y)\frac{1}{-D_{O^{2-}}}$$
 (A.16)

Substituting the above expression for dy/dx into Equation A.14 gives

$$\delta({}^{OX}\Delta^S\phi_e)/\delta x = -(\frac{z-2}{2(z-u)F})(\frac{1}{y^2})(\frac{d\Delta}{dt})(1-y)(\frac{\Delta G_{O^{2-}}}{D_{O^{2-}}})$$
(A.17)

Finally, substituting Equation A.14 into Equation 6.9 gives the following expression for the criterion of planar interface breakdown (for the case of electrochemical reductive dissolution of the oxide).

$$\delta^{OX} \Delta^S \phi / \delta x > -(\frac{z-2}{2(z-u)F})(\frac{1}{y^2})(\frac{d\Delta}{dt})(1-y)(\frac{\Delta G_{O^{2-}}}{D_{O^{2-}}})$$
(A.18)

Setting $\delta^{OX} \Delta^S \phi / \delta x$ equal to $-V/\Delta$ where V is the applied voltage and Δ is the film thickness, and rearranging gives

$$(V\Delta)(\frac{z-2}{2(z-u)F})(\frac{d\Delta}{dt})D_{O^{2-}} < (\Delta G_{O^{2-}})(1-y)(\frac{1}{y^2})$$
(A.19)

The left side of Equation A.19 contains the main processing parameters: the applied voltage, oxygen-ion diffusivity, and the oxide dissolution rate. The right side of Equation A.19 consists of the oxide composition, y, at the oxide/electrolyte interface and the free energy of formation of the array of oxygen anions. As summarized in Figure 6.5, the breakdown of interface planarity is promoted by small values of y, high values of the ratio of the oxide dissolution rates to the oxygen-ion diffusivity in the oxide, and low applied electric field in the oxide.

Appendix B

Criterion for Breakdown of Planar Oxide/Electrolyte Interface during Chemical Dissolution of the Oxide

In the event that the oxide does not undergo reductive dissolution, the stability of a negative perturbation in the planar interface will depend on chemical dissolution of the oxide. For this case, the stability of the planar interface during dissolution is related to the gradient of the chemical free energy (i.e., gradients in compositions of oxide and electrolyte). Specifically, if the driving force for dissolution of the oxide at the tip of a dent is greater than the driving force for the dissolution at the planar interface, the dent will be stable. Otherwise, the dent will be repaired and the planar interface will remain stable. (It should be noted that the dissolution of the oxide could be a combination of electrochemical reductive dissolution and chemical dissolution.)

The chemical dissolution of the anodized oxide in a fluoride-containing electrolyte is described by

$$M_y O_{z/2} + \frac{yz}{2} H^+ + yzF^- \to y(MF_z)_{aq} + \frac{yz}{2} OH^- + \frac{z(1-y)}{2} O_{OX}^{2-}$$
 (B.1)

where $(MF_z)_{aq}$ is the aqueous-phase complex composed of M^{+z} and F^- . The Gibb's freeenergy change for the chemical dissolution reaction is

$$\Delta G_D = \Delta G_D^O + RT \ln K_D \tag{B.2}$$

The equilibrium constant, K_D , of the chemical dissolution reaction is given by

$$K_D = \frac{[M^{+z}]^y (K_W)^{yu} [(O^{2-})_{OX}]^{z/2-yu}}{[M_y O_{z/2}] [H^+]^{2yu}}$$
(B.3)

In solutions with F^- , the F^- will complex the M^{+z} and cause a major decrease in $[M^{+z}]$, which will drive the dissolution reaction, Equation B.2, to the right.

Equations B.3 and B.4 indicate that $|\Delta G_D|$ increases (i.e., ΔG_D becomes more negative) with distance into the oxide from the oxide/electrolyte interface. The variation of ΔG_D with distance is a consequence of the changes in the oxides composition with distance. Because $[O^{2-}]_{ox}$ decreases while $[M_y O_{z/2}]$ increases with increasing distance, K_D decreases.

A dent in the planar interface will be stable if the value of ΔG at the tip of the dent is less (i.e., more negative) than ΔG_D at the planar interface. The criterion of instability of the planar interface during chemical dissolution of the oxide is presented in Equation B.4

$$\Delta G_{tip} < \Delta G_{plane} \tag{B.4}$$

where both sides of the inequality are negative. Equation B.4 defines the conditions that must be met to initiate dents/nanopores during anodization, when the dissolution of the oxide occurs chemically rather than by electrochemical reduction. While the chemical dissolution step does not directly depend on potential, the main external parameter is still voltage. Because ΔG_{tip} is determined by the variation of oxide composition with distance from the oxide/electrolyte interface, it is related to the condition of anodization (applied voltage). The right side of Equation B.4 represents the intrinsic properties of the materials involved in the anodization, e.g., the composition of the electrolyte (i.e., [H⁺]) and composition of the oxide (i.e., y).

Appendix C

Estimation of Nanopore and

Nanotube Spacing

The spacing of nanopores and nanotubes is an important characterization parameter which is easily measured experimentally. In this Appendix, the expression developed in the text for the minimum spacing of dents is evaluated. The minimum spacing of dents, λ_i , is less than the spacing of the fastest-growing, organized array of dents, λ_o (which is related to the spacing within organized arrays of nanopores and nanotubes). Thus, the calculated values of λ_i should be less than the measured values of λ_o , while the voltage dependence of λ_i and λ_o should be similar.

C.1 Reductive Dissolution of the Oxide

The expression for the minimum spacings of dents for the case of reductive dissolution of the oxide is presented in Equation C.1

$$(\lambda_i/2\pi)^2 = \frac{\Gamma}{\partial^{OX} \Delta^S \phi/\partial x - \delta^{OX} \Delta^S \phi_e/\delta x}$$
(C.1)

Estimates of λ_i are obtained by introducing appropriate values for the various terms in Equation C.1.

The Gibbs-Thompson coefficient, Γ , is given by

$$\Gamma = \gamma(MW)\rho ne \tag{C.2}$$

Solids	Environment	$\gamma ({\rm ergs/cm^2})$	Reference
Diamond (100)	Vacuum	5650 (calc)	Harkins [1942]
Silver	Vacuum	1140	Funk et al. [1951]
MgO	Vacuum	1200	Gilman [1960]

Table C.1. Surface Energies of Solids

Table C.2. Surface Energies of Liquid Mercury

Environment	$\gamma \ ({\rm ergs/cm^2})$	Reference
Vacuum	500	Zangwill [1998]
0.1 M NaCl (aq)	418	$Grahame \ [1947]$
0.1 M CaNO_3	423^{a}	Gilman [1960]

 a at potential of zero charge

where $\gamma = \text{oxide/electrolyte}$ interface energy. Tables C.1 and C.2 present a range of values for γ , demonstrating the influence of the identity of the solid and the surrounding environment on γ . For the calculation, it is assumed that $\gamma = 1000 \text{ ergs/cm}^2$ for the oxide/electrolyte interface. Because MW is the molecular weight of the oxide and ρ is the density of the oxide, $\text{MW}/\rho = 25.72$ for Al₂O₃, and 20.81 for TiO₂ (anatase). The number of electrons involved in the electrochemical reduction is defined as "n" (e.g., n = 2 for reduction of TiO₂ to $(\text{Ti}^{+2})_{aq}$). Substitution of the above values into the expression for Γ gives $\Gamma = 1.66 \times 10^{-8}$ V cm.

The denominator in the expression for $(\lambda_i/2\pi)^2$ consists of the difference between $\partial^{OX}\Delta^S\phi/\partial x$ and $\partial^{OX}\Delta^S\phi_e/\partial x$. Numerical values of $\partial^{OX}\Delta^S\phi/\partial x$ are estimated as follows.

C.1.1 Value of $\partial^{OX} \Delta^S \phi / \partial x$

 $\partial^{OX} \Delta^S \phi / \partial x$ is set equal to the ratio of the anodization voltage (V) to the thickness of the anodized oxide (Δ)

$$\partial^{OX} \Delta^S \phi / \partial x = -V/\Delta \tag{C.3}$$

The proper value of V/ Δ to insert into Equation C.1 is the value at which breakdown of the planarity of the interface begins. At this time, measurements of the oxides thickness when nanopores initiate have not been reported. Accordingly, a range of possible values of $\partial^{OX}\Delta^S\phi/\partial x$ is used instead, with the upper limit being 10⁹ V/m as that is the dielectric breakdown voltage.

C.1.2 Value of $\partial^{OX} \Delta^S \phi_e / \partial x$

An approximate expression for $\partial^{OX} \Delta^S \phi_e / \partial x$ (derived in Appendix A) is presented in Equation A.14, and reproduced here:

$$\delta({}^{OX}\Delta^{S}\phi_{e})/\delta x = (\frac{z-2}{2(z-u)F})(\frac{1}{y^{2}})(\frac{dy}{dx})(\Delta G_{O^{2-}})$$
(C.4)

The expression indicates that $\partial^{OX} \Delta^S \phi_e / \partial x$ is negative as $\Delta G_{O^{2-}}$ is positive and dy/dx is negative. That is,

$$\partial^{OX} \Delta^S \phi_e / \partial x = -A \tag{C.5}$$

where A is > 0. Finally, substituting Equation C.2 and C.5 into Equation C.1 yields

$$(\lambda_i/2\pi)^2 = \frac{\Gamma}{A - V/\Delta} \tag{C.6}$$

Briefly, λ_i is dependent on the electric field through the oxide and the composition of the oxide, as expressed in A, which is a function of y.

C.1.3 Compositional Gradient $(\partial y/\partial x)$ in the Oxide

The gradient of y is based in part on the minimum value of y (i.e., the value of y at the oxide/electrolyte interface, y(x = 0)) and the distance over which y increases from its minimum value at the interface to its maximum value of 1 in the interior of the oxide. This distance is the width of the space-charge region. Thus

$$\partial y / \partial x \approx \frac{\Delta y}{\text{width of the space-charge region}} = \frac{\Delta y}{x_{space-charge}}$$
 (C.7)

In principle, y can assume any value between 0 and 1:0 $\leq y \leq 1$. To form nanopores, however, y cannot be identically 0 or identically 1. For dissolution to occur, y must be greater than 0 and for dissolution to cause breakdown of the planar interface, y must be less than 1, 0 $\leq y < 1$. Further restrictions on the range of values of y can be made. Consider first the value of $\Delta y : y_{max} - y_{min} = 1 - y(x = 0)$. The value of $[M^{+z}]$ at the oxide/electrolyte interface, y(x = 0), fluctuates because of the effects caused by anodization and dissolution. Anodization consists of the oxidation of M to M^{+z} , which are added to the oxide at the metal/oxide interface. Simultaneously, O^{2-} are added onto the oxide at the oxide/electrolyte interface, so the value of $[O^{2-}]_{OX}$ at the outer surface increases and y decreases. The excess M^{+z} at the metal/oxide interface and the excess O^{2-} at the oxide/electrolyte interface have equal and opposite charge, so that the oxide as a whole is electrically neutral. O^{2-} at the outer surface are transported into the oxide toward the oxide/metal interface, and M^{+z} at the inner oxide surface are transported into the oxide toward the oxide/solution interface. For titanium (and other valve metals), the flux of O^{2-} is significantly larger than the flux of M^{+z} . [Davies et al., 1965; Mackintosh and Plattner, 1976] The ion migration raises the $[M^{+z}]$ at the outer surface and allows dissolution of the oxide, $M_y O_{z/2}$, into $y(MF_u)_{aq}$ and $yuOH^-$, and it creates excess O^{2-} on the surface of the oxide. The excess O_{OX}^{2-} in the outer surface diffuse/migrate into the oxide, raising the value of $[M^{z+}]$ and re-establishing a concentration at the surface of y(x = 0), which is greater than zero and less than unity. In evaluating $\partial^{OX} \Delta^S \phi_e / \partial x$, the concentration of M^{+z} as a function of x is approximated as varying linearly from a value of y(x = 0) at the oxide/electrolyte surface to a value of 1 at the edge of the space-charge region.

The width of the space-charge region is needed in order to estimate the gradient of y and is obtained from the work of *Fromhold and Kruger* [1973] and *Fromhold* [1977] who modeled the space-charge regions in oxides during anodization. For relatively thick films (100 nm) with high voltages (100 V), the space-charge region was approximately 10 nm wide. [*Fromhold*, 1977] For a 64 nm thick oxide (160 monolayers \times 0.4 nm lattice parameter) growing under a range of current densities, the space-charge region was approximately 15% of the overall thickness of the oxide, i.e., 9.6 nm thick. [*Fromhold and Kruger*, 1973] If specific anions such as fluoride were not present in the electrolyte, the dissolution of the oxide would be greatly reduced (and nanopores would not form). As such, 10 nm is a reasonable value of the width of the space-charge region for the conditions of anodization considered in the present study. In fact, XPS measurements by *Taveira et al.* [2005] indicate the space-charge region of titanium dioxide formed by anodization of titanium at 20 V is approximately 10 nm.

C.1.4 Value of $\Delta G_{O^{2-}}$

That the free energy of formation of the array of oxygen ions is positive is, perhaps, intuitively obvious. The value of $\Delta G_{O^{2-}}$ is determined with the aid of the following BornHaber cycle [Shen and Bursill, 1986; Weast, 1984]

$$(1/2)O_{2(g)} \to O_{(g)}(\Delta H = ((1/2) \text{ dissociation energy of molecular oxygen} = 2.57eV)$$

$$O_{(g)} \to O_{(g)}^{2-}(\Delta H = \text{ electron affinity of oxygen} = -7.28eV)$$

$$O_{(g)}^{2-} \to O_{(i)}^{2-}(\Delta H = \text{ interstitial oxygen ion in TiO}_2 = -8.58eV)$$

$$O_{(i)}^{2-} \to O_{(i)}^{2-} + (1/2)V_{Ti^{4+}}(\Delta H = \text{Ti}^{4+} \text{ vacancy in TiO}_2 = -40.29eV)$$

The result is $\Delta H_{O^{2-}} = 27$ eV. The latter is likely an upper limit of ΔH_O , because it is possible that traditional point defects are not present in Ti_yO₂. Assuming that "reconstructed" rather than "traditional" defects are formed in Ti_yO₂, as is the case for TiO_{2-x} (which has been the subject of theoretical analysis [Shen and Bursill, 1986] and transmission electron microscopic inspection, [Bursill et al., 1984]) the energy per added O²⁻ are less than 27 eV. Reconstructed interstitials and vacancies are thought of as aggregates of traditional defects. [Shen and Bursill, 1986] For example, the interstitial titanium defect that forms at high temperatures in nonstoichiometric TiO_{2-x} has a linear defect structure, and electrostatic interactions lead to clustering of the linear defects as the degree of nonstoichiometry increases. The free energy of formation of these extended defects per missing oxygen ion is less
than one-sixth smaller than that of a traditional titanium interstitial. [Shen and Bursill, 1986] Results of investigations of the Ti-S system also indicate extended defects rather than traditional point defects form in the TiS_{2-x} system. [Anderson, 1984]

In summary, there is no information available on the atomic structure of $\text{Ti}_y O_2$ but structural analyses of $\text{Ti}O_{2-x}$ and $\text{Ti}S_{2-x}$ suggest that reconstructed defects, rather than traditional point defects, are likely to form in $\text{Ti}_y O_2$. Accordingly, the value of $\Delta H_{O^{2-}} =$ 27 eV is likely an upper bound estimate. The use of $\Delta H_{O^{2-}} = 27$ eV in the calculations of minimum pore spacing (Figure 6.7a), λ_i , provides a lower bound estimate of λ_o . To illustrate the effect of $\Delta H_{O_{2-}}$ on the value of λ_i , calculations for the case in which $\Delta H_{O^{2-}}$ is set equal to 6.75 eV (=1/4 of 27 eV) is also presented in Figure 6.7b.

C.1.5 Electrolyte Compositional Gradients

The compositional gradients in the electrolyte are assumed, as a first approximation, to have a negligible effect on the gradient of the equilibrium potential. The gradient in $[H^+]$ in the electrolyte at the oxide/electrolyte interface is assigned the value calculated by *Macak* et al. [2005b] for the pH gradient down the length of nanopores in TiO₂.

$$\frac{\partial \ln[H^+]}{\partial x} = (4.606) \frac{\partial \log[H^+]}{\partial x} = -4.606 \frac{\partial pH}{\partial x} = \frac{-4.606(5-2)}{100 \text{nm}}$$
(C.8)

Substituting the above value of Equation C.8 gives the following as the contribution of the pH gradient to the overall gradient in the electrochemical potential: $\{\text{RT}/(z-u)F\}(4.606)(5 - 2)/100 \text{ nm} = 1.786 \times 10^{+6} \text{ V/m}$, which is small compared to the likely range of values of the anodization electric field, which are plotted on the horizontal axes of Figure 6.7 of the text.

C.2 Chemical Dissolution of the Oxide

As an alternative to electrochemical reductive dissolution, the anodized oxide film might dissolve chemically or by a combination of chemical and electrochemical mechanisms. It is important to recognize that the chemical dissolution of the oxide is indirectly dependent on the anodization voltage. The mechanism of dissolution does not require the presence of an electric field through the oxide (although the chemical dissolution may be field assisted). Instead, for chemical dissolution to break down the planar interface, a compositional gradient, $\partial y/\partial x < 0$, is required in the oxide. The compositional gradient, $\partial y/\partial x < 0$, is established by the anodization voltage. The necessity of an anodization voltage for breakdown of the planar interface during chemical dissolution is brought out in the following analysis of the change of the Gibb's free energy of the chemical dissolution reaction.

The chemical dissolution of anodized oxide in a fluoride-containing electrolyte is described by Equation B.1. The Gibb's free-energy change for the chemical dissolution reaction is presented in Equation B.2 and the equilibrium constant K_D for the reaction is given by Equation B.3, which is reproduced here:

$$K_D = \frac{[M^{+z}]^y (K_W)^{yu} [O_{OX}^{2-}]^{z/2-yu}}{[M_y O_{z/2}] [H^+]^{2yu}}$$
(C.9)

The gradient in the Gibb's free-energy change is then

$$\partial \Delta G_D / \partial x \approx RT (\partial \ln K_D / \partial x)$$

$$= RT \partial \{ y \ln[(MF_z)_{aq}] - yz \ln[F^-] - yz \ln[H^+] - \ln[M_y O_{z/2}] \} \partial x$$

$$= RT[(\partial y / \partial x) \{ \ln[(MF_z)_{aq}] - z \ln[F^-] - z \ln[H^+] - (1/y) \}$$

$$+ y \{ \partial \ln[(MF_z)_{aq}] / \partial x - z \partial \ln[F^-] / \partial x - z \partial \ln[H^+] / \partial x \}]$$
(C.10)

Because y is <1, and because each of the aqueous species have concentrations that are most likely <1 M, $(\partial y/\partial x)\{\ln[(MF_z)_{aq}] - z\ln[F^-] - z\ln[H^+] - (1/y)\}$ likely outweighs $y\{\partial \ln[(MF_z)_{aq}]/\partial x - z\partial \ln[F^-]/\partial x - z\partial \ln[H^+]/\partial x\}$. Consequently,

$$\partial \Delta G_D / \partial x \approx RT (\partial y / \partial x) \{ \ln[(MF_z)_{aq}] - z \ln[F^-] - z \ln[H^+] - (1/y) \}$$
(C.11)

Furthermore, $\partial y/\partial x$ is <0; the three terms of the form ln[concentration] are all <0, and $(-z \ln[F^-] - z \ln[H^+])$ is positive, and most likely $(\ln[(MF_z)_{aq}] - z \ln[F^-] - z \ln[H^+])$ is also positive. Consequently, for $\partial \Delta G_D/\partial x$ to be positive |1/y| must be greater than $(\ln[(MF_z)_{aq}] - z \ln[F^-] - z \ln[H^+])$. That is, in order to form dents, y must be significantly less than 1, as was the case for formation of dents by electrochemical reductive dissolution. In addition, each of the terms, including $\partial y/\partial x$, is dependent on anodization voltage, but the form of the dependence is not yet known. For the planar interface to break down, 1/y(x = 0)must be the dominant term inside the {} brackets. Consequently, the voltage dependency of $\partial \Delta G_D/\partial x$ is proportional to $\partial y/\partial x \{B - 1/y(x = 0)\}$, where B is a positive number and y(x = 0) decreases as V increases. That is, a large anodization voltage creates a large deficit of metal cations on the outside surface of the oxide. Assume that $y(x = 0) \approx 1/(\alpha V + 1)$, where α is a constant, and $\partial \Delta G_D/\partial x \approx RT(\partial y/\partial x) \{B - 1 - \alpha V\}$. Thus, for chemical dissolution, the spacing of dents is given by

$$\lambda_i = \frac{\Gamma}{RT(\partial y/\partial x)(B - 1 - \alpha V)} \tag{C.12}$$

which is similar to the form of the expression for nanopores spacing in the case of electrochemical reductive dissolution. The breakdown of the interface requires a critical minimum value of y(x = 0), and the spacing of dents (nanopores) increases as the voltage increases.

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