TITANIUM DIOXIDE DIELECTRIC LAYERS MADE BY ANODIZATION OF TITANIUM: THE EFFECT OF DISSOLVED NITROGEN AND OXYGEN

by

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Titanium Dioxide Dielectric Layers Made by Anodization of Titanium: The Effect of Dissolved Nitrogen and Oxygen

Abstract

by

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This work investigates improving the dielectric structure and properties of TiO$_2$ formed by anodization of nitrogen-and-oxygen-infused Ti substrates for electrolytic capacitors. The controllable parameters of the diffusion process and the anodization were studied to evaluate the effect of nitrogen and oxygen dissolved in the Ti substrate on the formation of the anodic oxide and its properties, particularly the leakage current density. The best diffusion treatment condition to decrease the leakage current density for Grade 1 Ti was found to be infusion at 1133 K (860 °C) for 22 ks. Under this condition, nitrogen and oxygen were managed to infuse into Ti as interstitial solutes without the formation of Ti oxides or nitrides. The increased solute concentration was measured by XRD. Moreover, concentration—depth profiles were recorded by XPS. SEM-XEDS and TEM-XEDS were used to characterize the structure and composition of TiO$_2$. The presence of nitrogen could interfere with formation of crystalline oxide and contributes to an amorphous TiO$_2$ layer. The formation of an amorphous oxide layer is beneficial for reducing the leakage current density. The results show that nitrogen and oxygen
dissolved in Ti substrate can significantly lower the leakage current density of TiO₂ formed by anodization. The microscopic mechanisms of oxide growth and leakage current are discussed, particularly with regard to the presence of nitrogen and oxygen, to explore the potential of solutes in the Ti substrate for improving the dielectric properties of the Ti oxide layer. It was found that the nitrogen atoms, as the main interstitial solute, interfere with the diffusion of oxygen through the TiO₂ layer and therefore interfere with the growth of dielectric layer. As a result, the population of structural defects that enable leakage current is significantly reduced.
1. Introduction

1.1 Purpose of Work

A promising candidate for the dielectric layer of electrolytic capacitors is TiO$_2$ (titanium dioxide). This material has several distinct advantages: high dielectric constant, high electric field strength suitable for high voltage applications, high capacitance for energy storage over current commercial capacitors, and self-repair ability in oxidizing electrolyte. However, TiO$_2$ also suffers from high instability, gradual loss of capacitance (especially at elevated temperature), and high leakage current density.

While it was recognized early on that structural defects in the TiO$_2$ dielectric layer can cause significant leakage current densities, preliminary experimental evidence has shown that the presence of solute atoms in the to be anodized Ti substrate can improve the dielectric properties of the TiO$_2$ layer formed by anodization. The purpose of the present work was to explore whether the properties can be improved by oxygen and nitrogen dissolved in the Ti substrate before anodization.

The approach pursued in this project to reduce the leakage current density is to explore the effect of infusing the Ti substrate with nitrogen and oxygen from a gas phase prior to anodization. The goal was to generate a homogeneous, uniform solid solution of nitrogen and oxygen in the Ti substrate without forming second phases (Ti oxides or nitrides). After the infusion treatment, the TiO$_2$ was formed by anodization. A systematic study was performed on the diffusion parameters (temperature, time) to
evaluate the effect of nitridation and the structural analysis of the anodic oxide in order to find the best conditions for decreasing the leakage current density and to understand the microscopic mechanisms of leakage current and anodic oxide growth.

1.2 Capacitors

1.2.1 Electrolytic Capacitors

A capacitor is an electric device that can store electrostatic energy when charged to generate an electric field across the dielectric layer. Although the actual size and form of a capacitor may vary, a typical structure of a capacitor involves two electric conductors and one dielectric layer to separate them as an insulator.

An electrolytic capacitor is one that uses an ionic conducting liquid, also known as electrolyte, as one of the electrodes. A big advantage of the electrolytic capacitors is the large anodic surface that they provide. A thin oxide layer usually forms between the electrolyte and the other conductive plate as a dielectric layer separating the two conductors. The large plates and the thin dielectric give a much larger capacitance per unit volume. Owing to its capability of storing more energy than other capacitor forms, an electrolytic capacitor can be particularly useful for, e.g., power supplies.

1.2.2 Capacitance, Energy Density and Leakage Current of Capacitors

Capacitance, by definition, is the charge storage ability per unit voltage applied across the capacitor plates. The capacitance $C$ of a parallel-plate capacitor can be calculated as
\[ C_{\text{dielectric}} = \frac{\varepsilon_0 \varepsilon_r A}{d}, \]  

where \( \varepsilon_r \) is the relative static permittivity (dielectric constant), \( \varepsilon_0 \) is the constant electric permittivity \((\varepsilon_0 \approx 8.854 \times 10^{-12} \text{ F} \cdot \text{m}^{-1})\), \( A \) is the area of overlap of the two plates, and \( d \) is the separation between the plates.

The energy of the electric field in a capacitor charged to a voltage amounts to

\[ E = \frac{1}{2} CU^2, \]  

where \( C \) is the capacitance of the capacitor and \( U \) is the applied voltage.

The energy density \( u \) of a dielectric layer is defined as the amount of energy stored per unit volume \( V \) of the layer

\[ u = \frac{1}{2} \frac{CU^2}{V}. \]  

If a voltage is applied between the electrodes of the capacitor, certain features of the microstructure of the TiO\(_2\) dielectric layer act as regions of increased electric conductivity, which give leakage current. A high density of such structural defects can lead to intolerable high leakage current density. The leakage current through a capacitor is typically time-dependent and affected by the applied voltage, temperature, dielectric property, and capacitance. Normally, the leakage current density decreases with reduced voltage or temperature and is proportional to the capacitance value. When there are structural defects, the dielectric layer no longer has negligible conductivity.
high leakage current density is a performance disadvantage of capacitors and may lead to several issues in technical applications. A constant current flow may slowly discharge the capacitor and generate heat, which eventually cause dielectric breakdown. Reducing the leakage current density is one of the important methods to extend capacitor life and to improve its performance.

1.2.3 Commercial Electrolytic Capacitors

For commercial applications, the most commonly used electrolytic capacitors are based on Al or Ta. In these capacitors, anodic Al2O3 and Ta2O5 are used as the dielectric oxide film respectively.²

![Fig. 1-1: (a) Al electrolytic capacitors. (b) Ta electrolytic capacitors.](image)

Al electrolytic capacitors (Fig. 1-1 (a)) are inexpensive and can work at up to 500 VDC and at low frequencies. This type of capacitors uses pure Al as conductive plates and Al oxide as a dielectric layer. The working range of such Al capacitors is from • 1μF to 1 F.
For Ta capacitors (Fig. 1-1 (b)), the spongy Ta plate gives a dramatically increase in surface area to enable larger capacity of energy storage. Ta capacitors only work at relatively low voltage (up to 100V) but have a high tolerance of operating temperature (up to 125°C). Ta electrolytic capacitors are suitable for portable electronic devices like cell phones, portable music players and personal computers.³

Ta capacitors have better performance and longer operational life than Al capacitors but are more expensive. As compared to the dielectric constant of Ta₂O₅(12×10⁶Hz), TiO₂ has even higher dielectric constant (85×10⁶Hz) and much lower production cost⁴ which makes Ti a very promising substitutive material of electrolytic capacitor application.

1.3 Ti and Ti Oxide

1.3.1 Structure of Ti and TiO₂

Ti (atomic no. 22) is a silver-colored transition metal. It is the 9th most abundant element in the earth’s crust. At room temperature, pure Ti has a single phase HCP (hexagonal close-packed) crystalline structure (α-Ti). At 1155K (882°C) it transforms to BCC (body-centered cubic) crystal structure known as β-Ti.

TiO₂ (titanium dioxide), also known as titania, naturally exists in three mineral forms: rutile, anatase and brookite. Two of them, namely rutile and anatase, have tetragonal crystal structures while brookite is an orthorhombic crystal. In thermal stability, the metastable anatase and brookite are expected to convert to rutile upon heating.
because rutile is the equilibrium phase at all temperatures. The density of TiO₂ varies from 3.84 g·cm⁻³ (anatase) to 4.23 g·cm⁻³ (rutile).

The lattice parameters of α-Ti are \(a₀=2.95 \times 10^{-10} \text{ m}\) and \(c₀=4.68 \times 10^{-10} \text{ m}\). The lattice parameters of rutile is \(a₀=4.59 \times 10^{-10} \text{ m}\) and \(c₀=2.96 \times 10^{-10} \text{ m}\). The lattice parameters of nanocrystalline anatase is \(a₀=3.79 \times 10^{-10} \text{ m}\) and \(c₀=9.51 \times 10^{-10} \text{ m}\).

The atomic mass of Ti is 47.9 and its density is 4.51 \(\times 10^6 \text{ g/m}^3\). And the molar mass of TiO₂ is 79.866 g/mol and the density of TiO₂ is 4.23 \(\times 10^6 \text{ g/m}^3\).

1.3.2 Current Applications of TiO₂

Although Ti has gained great attention in many research and industrial fields, only about 5% of the world's annual production of titanium minerals is used for making Ti alloys whereas the rest 95% is used for TiO₂ products.

TiO₂ is the most commonly used white color pigment for paints, paper, plastics, rubber, and various other products because of its white color, high refractive index, and light-scattering ability. Since the 1970's, studies on the photocatalytic properties of TiO₂ have been pursued actively. These days TiO₂ is used as a photosensitiser for photovoltaic cells, and an electrode coating in photo-electrolysis cells to enhance the efficiency of electrolytic splitting of water into hydrogen and oxygen. There are companies that specialize in manufacturing high-purity TiO₂ products, meant for electronic devices including multilayer ceramic capacitors, PTC thermistors and dielectric resonators.
These electronic grades of TiO$_2$ are characterized by high purity and high dispersibility and are produced by gas phase reaction of titanium tetrachloride with oxygen.$^{10}$
2. Background

2.1 Dielectric Properties of TiO₂

From a sketch of dielectric properties and energy densities data (Fig.2-1), the dielectric constant of anodic TiO₂ is up to 150 and is much higher than the anodic Al₂O₃ (about 10) and anodic Ta₂O₅ (about 20-30). The structure of the dielectric layer affects significantly on the dielectric strength, and the crystalline structure of oxides have much lower dielectric strength than amorphous structure (commonly made by anodization). The energy density of amorphous TiO₂ could be up to 10 times larger than amorphous...


Ta$_2$O$_5$ and amorphous Al$_2$O$_3$. Since crystalline oxides have line-and-boundary defects that are not repairable, they can operate only at energy densities that are reduced to 0.01-0.25% of theoretical values. The reported dielectric strength of TiO$_2$ is 40-85 kV/cm, which is slightly higher than Ta$_2$O$_5$ (25-70 kV/cm). 4 Usually, a pure Ti surface anodized to 10 or 20 V has a capacitance respectively of 5.0 μF/cm$^2$ or 2.5 μF/cm$^2$. 2

Although TiO$_2$ has higher dielectric constant and higher energy density, it suffers higher leakage current density than Al and Ta so the pure Ti could not be used for commercially electrolytic capacitor anode. For instance, the leakage current density of undoped-TiO$_2$ is normally above 100 μA/cm$^2$ under 100 V while the operating leakage current for commercial electrolytic capacitors is 5-10 μA/cm$^2$. Constant exposure to heat when the capacitor operates can cause TiO$_2$ breakdown and excessive leakage. A Ti capacitor will self-degrade if unused for a period, or have some permanent damage when it may short circuit after experiencing high leakage. A leaky capacitor can cause the grid circuit voltage to be raised from its normal bias setting, causing excessive current or signal distortion in the downstream tube. 12

Overall, the high leakage current density caused by structural imperfection of the TiO$_2$ dielectric layer are the mainly reasons preventing Ti electrolytic capacitors from commercially usage. The reduction of the leakage current density by improving the dielectric microstructure is of great importance for Ti electrolytic capacitors.
2.2 Anodization of Ti

Typically, a thin dielectric oxide is formed on the surface of the metal anode by an anodizing process, with cations provided by the metal and anions provided by an electrolyte.

Fig.2-2: Schematics of the evolution of the cell current \( I \), the cell voltage \( U \) and the film thickness \( h_f \) for a galvanostatic, a potentiostatic and a potentiodynamic anodization process.\(^{13}\)

The anodization is carried out by applying an external power source to force a current to flow from an anode to a cathode. Anodization can be conducted in 3 different modes, illustrated in Fig.2-2: (a) Galvanostatic mode, characterized by imposing a constant current. (b) Potentiostatic mode, corresponding to a constant voltage being applied between anode and cathode. (c) Potentiodynamic mode, which – in the present context – means to increase the voltage by a controlled rate.

Under galvanostatic conditions, the oxide growth rate is proportional to the imposed current density when the oxide grows at a constant rate without side reactions or structural transformation, which gives a constant rate of voltage increase. The applied
voltage increases proportionally with the thickness of the oxide. But in reality, the oxide transforms from amorphous to crystalline during anodization, and subsequently the voltage is not increased linearly. Galvanostatic growth is sometimes followed by a potentiostatic aging at the final voltage possibly for improving the stability of the oxide, which is found to further grow the oxide and promote crystalline oxide.¹³

Fig. 2-3 shows two possible ways to form new oxide after the formation of first monolayer of oxide. These two types of oxide grown mechanisms under different conditions are both discussed in literatures about TiO₂ so the overall mechanism for TiO₂ grown by anodization remains to be controversial. If the film grows by migration of cations from the metal/oxide interface outwards, new oxide will be formed at the oxide/electrolyte interface. In contrast, the oxide film will grow mainly at the metal/oxide interface if inwards anionic transport is dominant.¹³

![Diagram of oxide growth](image)

Fig. 2-3: Illustration of the influence of the type of ionic transport on the location of new film growth ¹³
The distribution of different crystal structures of TiO$_2$ is related to the ionic transport during anodization. There are two classes of models explaining the kinetics of anodic oxide growth: high-field model and low-field model. According to the high-field theory, the ionic current density is associated with the migration of one type of ion and the contribution of diffusion to the ion transport is negligible due to the strong electric field. On the contrary, the low-field model assumes that the effective electric field in the oxide film is low and the contribution of diffusion and low-field migration must be both taken into account. There are still controversies about the oxide growth models and mechanisms. Habazaki reported that the anodic film formed one outer amorphous region and one inner crystalline region (anatase structure) by applying constant current density on sputtering-deposited Ti-Al and Ti-Si alloys, and postulated that the outer region was formed at film/electrolyte interface by mainly outward migration of Ti$^{4+}$ while inner region was formed by inward migration of O$^{2-}$ ions.$^{14}$ A similar two-layer structure of anodic oxides has also been observed on Al-Hf alloys,$^{15}$ Ti-W alloys,$^{16}$ and Ti-Mo alloys.$^{17}$

2.3 Diffusion Treatment

2.3.1 Current Work of Diffusion Treatment of Ti

Diffusion treatment usually infuses interstitial solutes into the base material to cause surface hardening. Surface hardening of Ti by infusion with nitrogen, for example, is a well-known technique that is analogous to the carburization of stainless steels at low temperature.$^{18}$ However, most of these nitriding techniques have the risks of forming
second phases, such as Ti nitrides, owing to the high affinity of Ti for nitrogen. However, the formation of second phases is usually not desirable because they compromise mechanical properties and corrosion resistance of Ti alloys. In spite of the high stability of Ti nitrides, a new method, named “kinetically controlled nitridation”, could be developed to allow nitrogen infusion without formation of Ti nitrides to build up a large interstitial solute concentration by nitriding under a very low nitrogen activity. For a 10μm homogeneous diffusion depth with a maximum 8at.% of nitrogen concentration near the surface, the Ti surface hardness has gained a 100% increase and the large interstitial concentration has caused a phase transformation from β-Ti to α-Ti. A similar hardness improvement has also been observed in Ti-6Al-4V. The new method of nitridation under kinetic control of nitrogen activity operates in a non-equilibrium regime at low and controlled nitrogen partial pressure, established by metal—metal-nitride powder pack. The nitrogen partial pressure can be controlled by the temperature of the powder pack. The results of Ti-6Al-4V samples under the kinetically-controlled nitridation shows that the surface hardness increased from 350HV to 800HV50 with up to 10at.% nitrogen in a 10μm infused case after a 260ks nitridation with Cr-CrN powder pack. The nitrided Ti-6Al-4V shows sufficient ductility, which is confirmed by TEM studies revealing dislocations at the environments of hardness indents that were made in the TEM specimen.

Besides nitridition for surface hardening, the doping of 4H-SiC with nitrogen was reported to have an effect on reducing the thermal activation energy of nitrogen at the hexagonal site by 50% through increasing the nitrogen concentration by a factor of
Nakamura found that nitrogen infusion of Ta can dramatically improve the leakage current density of dielectric layers made by anodizing of Ta. Increasing the nitrogen concentration to $10^{21}-10^{22}$ atoms/cm$^3$ can reduce the leakage current density of Ta oxide by a factor of $10^5$ while the annealing could only reduce the leakage current density to half.\textsuperscript{22}

2.3.2 Current Work of Nitrogen Infusion of TiO$_2$

Nitriding of TiO$_2$ has been widely applied for improving the photocatalytic properties of TiO$_2$. It was observed that the doping TiO$_2$ with nitrogen (and Sm) yielded much higher photocatalytic activity than pure TiO$_2$ under visible light. This was attributed to increased crystal size and reduced density of grain boundaries, which enables more efficient separation of electrons and holes on Sm/N-TiO$_2$.\textsuperscript{23} Kim reported that ordered N-doped TiO$_2$ nanotubes grown on N-rich phase of Ti alloys had smaller diameter than the ones grown on the low N-concentration phase.\textsuperscript{24}

Research done by Ki found that nitrogen and oxygen doping of Ti surface layer enables the growth of a doped anodic Ti film and can decrease leakage current density of Ti anodic film. Also the leakage current density of Ti anodic film decreases with higher N/ O doping level.\textsuperscript{2}
Fig. 2-4: Ti—N Phase diagram. 

Fig. 2-5: Ti—O Phase diagram.
The Ti—N phase diagram (Fig.2-2) exhibits the considerable solubility of nitrogen in α—Ti: up to 23 at% at 1223 K (1050°C). The solubility of β phase has a maximum of 7 at%. At 1155 K (882°C), Ti undergoes a HCP to BCC (α–β) phase transformation. The Ti—O phase diagram (Fig.2-3) shows that the solubility of oxygen can be up to 33 or 8 at% in α and β-Ti, respectively. Since the solubility of both nitrogen and oxygen in β phase is considerably lower than in α phase, the desirable temperature for nitrogen and oxygen infusion should be just below the transition temperature from HCP to BCC, i.e. about 882°C. And the presence of nitrogen and oxygen may increase the transition temperature by stabilizing the HCP phase.

2.3.3 Diffusion Coefficient

The diffusivity, or diffusion coefficient, $D$, is defined by Fick’s First Law ($J = -D \frac{\partial \phi}{\partial x}$).

Usually, since diffusion is a thermally activated microscopic process, the diffusion coefficient follows an Arrhenius type relationship as a function of temperature

$$D = D_0 \exp\left(-\frac{Q}{RT}\right),$$

where $D_0$ is the pre-factor (a temperature-independent pre-exponential constant), $Q$ is the activation energy for the diffusion, $T$ is the absolute temperature, and $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$).

For diffusion of nitrogen in pure Ti, $D_0$ and $Q$ were measured by Wood in 1974 that $D_0=0.8*10^{-4}$ cm$^2$s$^{-1}$ and $Q=2.2X10^{-4}$ J at given temperature range of 1073 to 1773 K.$^{26}$
2.4 Characterization of Anodic TiO$_2$

A wide variety of analytical techniques has been used to evaluate the thickness, morphology, chemical composition, functional and mechanical properties of the anodic oxide. For instance, Auger depth profiling or XPS (x-ray photoelectron spectroscopy) depth profiling could give an accurate thickness measurement of the oxide to the thickness range of nanometers up to hundreds of nanometers. TEM could provide information about oxide morphology and crystal structure, while AFM (atomic force microscopy) or STM (scanning tunneling microscopy) have been used to study the pores or cracks in the oxide as well.

2.4.1 Microstructure of Anodic Oxide

Anodic TiO$_2$ is usually reported to be initially amorphous, then to crystallize progressively (with respect to time or a critical thickness) to the anatase structure. Under appropriate conditions, either a fully amorphous oxide layer or a fully polycrystalline oxide could be obtained. There are studies reporting that at particularly low rate of oxide growth no amorphous layer forms at the beginning.

The TEM study of anodic oxide as the anode for lithium ion batteries done by Lindsay revealed that the anodized oxide mostly consists of amorphous oxide with small inclusions of crystals.$^{27}$
Fig. 2-6: TEM of a FIB-milled un-cycled film in cross-section. (a) Bright-field image. (b) High-resolution image and selected-area diffraction pattern.

Fig. 2-7: (a) Transmission electron micrograph of an ultramicrotomed section of the aged Ti–6at%Si alloy specimen anodized to 120 V at 50 Am⁻² in 0.1 mol dm⁻³ ammonium pentaborate electrolyte at 293 K. (b) High-resolution image of a film region containing voids.
The TEM results of Habazaki published in 2003 showed voids inside the anodic film caused by O$_2$ gas due to a high anodizing voltage. A similar behavior of O$_2$ void formation was also found in Ti-W alloy.$^{28}$

2.4.2 Functional Characterization of Anodic Oxide

The evaluation of certain functional (electric) properties of the anodic oxide is of great importance for specific applications. There are some important parameters to evaluate the performance of a capacitor material: RC time constant, frequency, maximum voltage and temperature for permanent technical applications, and lifetime in service.

The RC time constant, $\tau$, is equal to the product of the circuit resistance $R$ and the circuit capacitance $C$

$$\tau = RC = \frac{1}{2\pi f_c}, \quad (4)$$

where $f_c$ is cutoff frequency.

The dielectric constant of the anodic oxide films to be used as dielectrics can be determined by EIS (electrochemical impedance spectroscopy). However, measurements by Ki showed that the behavior of TiO$_2$ deviates from that of the ideal dielectric, which may come from semi-conducting behavior of a portion of the anodic oxide.$^2$ For TiO$_2$, the conduction band is accessible for the lower oxidation state and close to the valence band, while the valence band is composed of filled O 2p states, which gives a small band gap of about 3 eV.$^{29}$ It is reported that the conductivity of an undoped TiO$_2$ is increasing with decreasing oxygen partial pressure, indicating oxygen-deficiency (n-type
conductivity). In amorphous TiO$_2$, the bandgap is replaced by a trail of localized states within the bandgap, which is larger than the bandgap of crystalline oxides, so the direct injection of electrons is expected to be more difficult. Therefore, the structural defects of TiO$_2$ are critical in determining the dielectric properties.
3. Experimental Procedures

3.1 Materials

3.1.1 Ti raw materials

All experiments in this thesis used grade 1 (commercially pure) Ti wire supplied by Perryman Company. The wire had a rectangular cross-section with a width of 1 mm and a thickness of 0.52 mm. It was wrapped in a coil.

3.1.2 Chemicals

For these experiments, nitric acid (69%), sulfuric acid (95.5%), acetic acid (99.7%), hydrofluoric acid (49%) and perchloric acid (70%) were procured from Fisher Scientific. Bromine (99.5%) was purchased from Sigma-Aldrich.

3.1.3 Furnaces

Two different furnaces were used in this work. One was a horizontal clam-shell style tube furnace with a maximum operating temperature of 1373 K (1100 °C). The other one was a vertical tube furnace with a maximum operating temperature of 1473 K (1200 °C). The furnaces were tested on temperature accuracy and recalibrated to make sure the temperature difference was no larger than 3 K within the working zone (15-20 cm). Generally it takes up to 1 ks (60 min) for the vertical furnace to heat up to the diffusion temperature (973 K, 1073 K, 1133 K, 1173 K or 1273 K) and about 0.25 to 0.50 ks (15-30 min) for the horizontal tube furnace.
3.2 Sample Surface Preparation

3.2.1 Mechanical Polishing/Sanding

Grade 1 Ti wires were polished on both sides with SiC (silicon carbide) sandpaper up to P2400 grit size and cut into 5cm long samples. The purpose of the mechanical polishing was to remove natural TiO\textsubscript{2} from the surface of the wires and to eliminate other possible contaminations during the production process. The natural oxide that formed when the raw materials were exposed to air was about 5nm thick. After polishing, the samples were ultrasonically cleaned in acetone for at least 0.6ks (10min) to remove possible sandpaper residues.

3.2.2 Chemical Etching

Even after having been polished with sandpaper, the Ti wires could still have had surface contaminations. To remove the damaged surface layer, decrease the surface roughness, and obtain a clean, smooth surface for further treatments, the specimens were wet-chemically etched. All etching work was done on polished samples.

HNO\textsubscript{3} (nitric acid) etching on polished Ti wires was performed under a variety of conditions. The concentration of the acid was varied from 10 to 50%, and the etching time was varied from 15 to 600s. Subsequently, the wires were rinsed with deionized water.
After polishing with SiC paper, the Ti wires were immersed into a 10 or 50% H₂SO₄ solution for 15, 30, or 300s.

Acetic acid was also used as a chemical solution for cleaning sample surfaces. In this procedure, diluted (10%) CH₃COOH (acetic acid) as well as pure CH₃COOH was applied for 15 or 30s.

HF (hydrofluoric acid) is known as a powerful etchant for Ti and Ti alloys. However, the experiments on HF polishing solution showed either uniform etching or a Ti oxide film formation. Some industrial facilities have introduced a HF–HNO₃ solution (5% HF mixed with 10% HNO₃), which gives a controlled etching rate. In this project, the desired acid concentrations were found in the range of 3 to 10 vol% (about 1.5 to 5 at %) for HF and 10% to 20% for HNO₃.

3.2.3 Electropolishing

Many papers have reported that a clean, bright, and flat surface of Ti or Ti-based alloys is obtained by electropolishing in various mixed acid solutions.⁴,³²,³³,³⁴,³⁵ In the course of the present project, several electropolishing solutions were tested.

All Ti wires was cut into 50mm long specimens with Ti nitride coated scissors followed by mechanically polishing with sand paper to prevent undesired contamination. Each Ti specimen was immersed in an electrolyte bath which served as an anode. Two pure Ti stripes were used as a cathode, yielding a surface area ratio of about 10:1. The electrodes were connected to a DC power supply. In a typical electropolishing process,
the metal surface on the anode is oxidized and dissolved, while the cathode reaction releases hydrogen gas. In order to reduce the amount of hydrogen absorbed in the anode, a cooling bath was prepared with commercial antifreeze (an ethylene glycol-based solution) and the temperature of the bath was held at −11°C. The electropolishing tests were performed both in room temperature and −11°C.

![Schematic of electropolishing](image)

**Fig. 3-1:** Schematic of electropolishing.

Based on previous research done by Chou, electropolishing on pure Ti was performed in the following solution: 50 ml HClO₄ (perchloric acid, 70%), 350 ml butanol, and 600 ml methanol. The experiment succeeded with a voltage of 28 V DC and a current density of 0.1 A/cm². The temperature varied between −35 and −40°C. The Ti samples were electropolished in this solution for 240 s in a beaker with 300 rpm stirring.

In the present project, all above-mentioned experimental conditions were fulfilled except the polishing temperature. The lowest temperature reached was −11°C, due to equipment limitation. So the samples were divided in two groups and electropolished at
room temperature or at −10°C. A voltage range of 15-30V DC and a current density of 0.1-0.2A/cm² were combined for the different polishing rates.

A perchloric acid-acetic acid solution was mentioned by Vander Voort and used for pure Ti and alloys.³⁴ The solution contained 5ml perchloric acid and 80ml acetic acid. The acid mix was used at 20-60 V DC and the samples were polished for 60-300s.

Another method for electropolishing pure Ti was published in Vander Voort’s book.³⁴ The etching solution was made by mixing 35ml perchloric acid with 390ml methanol, 350ml ethylene glycol and 25ml distilled water. The operation voltage was 30V DC and the current density was set at 0.2A/cm². Ti specimens were electropolished at room temperature and −10°C and held in this solution for up to 120s.

A mixed solution with 500ml methanol and 100ml H₂SO₄ was prepared for electropolishing Ti and Ti Alloys. In this experiment, the voltage was set at 20V and a current density of 0.2A/cm². The specimens were electropolished in solution at room temperature or −10°C for 20s then immediately washed with ethanol to remove the residues.

The electrolyte contained 500ml ethanol and 100ml H₂SO₄. Similar to previous conditions, two groups of samples were tested under 0.2A/cm² for 20s in room temperature acid solution and −11°C electrolyte, but with a stable 8V voltage instead of 20V.
Barker reported an electropolishing procedure under room temperature for a Ti–6Al–4V alloy by making an electrolyte with 40ml sulfuric acid, 13ml hydrofluoric acid and 8ml glycerin. According to his thesis, a current density of 1A/cm² and a DC voltage of 20V were implemented. Comparison groups of specimens were prepared by changing the time from 15 to 60s.

In 2008, Bohme and Piesslinger-Schweiger filed a patent about a new method for electrochemical polishing of surface of Ti or Ti-based alloys. 99 wt. % methane-sulfonic acid with 1% etidronic acid was used as polishing solution. Ti wires were polished in this solution at 10 to 28V for 240 to 420s.

3.3 Encapsulation (Retort Making)

Grade 2 Ti tubes were cut from 2m long Ti round tubes with a stainless steel tubing cutter. The small tube was 15cm long and had an inside diameter of 1.1cm, corresponding to an inner cross-section of 52 cm² and a volume of 14 cm³. Then the tube was cleaned in an ultrasonicator with acetone inside and out to reduce contaminations. The samples, after cleaning, were spot-welded on a 10cm folded Ti getter wire to prevent them from touching the tube. After the samples were inserted, both ends of the tube were closed by a mechanical press and welded using an argon arc welding torch to avoid air leakage.

3.4 Infusion of Interstitial Solutes

3.4.1 N₂ and O₂ Diffusion
When the Ti retort was welded in air, the naturally provided amount of air (primarily 80% N₂ and 20% O₂) was trapped inside the tube and used as N₂ and O₂ source to dissolve into the sample. Based on the size of the Ti retort, there were approximately 4.7x10⁻⁴ mol N₂ and 1.2x10⁻⁴ mol of O₂ in the retort at 25°C.

The sealed Ti retort was put in a one-end sealed stainless steel tube (1.5 m long, 2.5 cm in diameter), which with the other end was attached to a mechanical pump to keep the inner pressure of the stainless tube around 2 Pa. The purpose of this double tube design is to avoid oxidation and to reduce the amount of air that may diffuse through the Ti tube during the long time heat treatment in the vertical furnace.

The vertical tube furnace was set at various temperatures (700, 800, 860, 900, or 1000°C) and held for three different time intervals of 5, 22, and 86 ks (1.5, 6, and 24 h) at each temperature to allow gas–solid diffusion. After heat treatment, the samples were cleaned again with ethanol and ready for anodization.

3.4.2 N₂ Diffusion

In the preliminary tests, efforts were made to separate the effect of nitrogen from diffusing oxygen simultaneously. In order to reduce the amount of O₂ in the retort, 0.2 g of Ca or Mg was put in the bottom of the retort to react with O₂ during the heat treatment. A cleaned Ti strip (50 mm × 5 mm, 200 µm thick, commercially pure) was spot-welded on a 10 cm folded Ti getter and was placed into the double retort. During the nitrogen infusion process, the furnace temperature was held at 800°C for 7 ks. Then the
retort was cut open and the Ti strip was removed from the getter and immersed in 1% HNO₃ solution to leach out the CaO or MgO formed on the surface.

An ultra-high vacuum system was built to try to dissolve nitrogen into Ti without adding any reduction agent. Basically, the samples were placed in a one-end closed fused-SiO₂ tube (2.5 cm in diameter). The other end of the tube was sealed with O-rings and attached to a turbo pump and a high-purity N₂ tank. The SiO₂ tube was put in the clam-shell style tube furnace for heat treatment after pumping out of the air in the tube. When the furnace reached the targeted temperature (700°C or 800°C), the turbo pump would be turned off and a small amount of nitrogen would be purged into the tube to diffuse nitrogen solely into the samples.

3.5 High-Vacuum Annealing

Since the N/O infusion treatment can be considered as a diffusion process and a simultaneous annealing process, it is important to study the annealing effect and compare the results of tempered samples with diffusion-treated ones. The experiments designed for annealing used a similar ultra-high vacuum system, but without a nitrogen valve. The pressure was maintained around 10⁻⁴ Pa. Since the results of annealed samples were used for comparison with N/O-diffused samples, the Ti samples were heated to same temperatures as they were heated in the diffusion experiments. Subsequently, they were anodized under same conditions as the N/O-diffused samples.
3.6 Anodization

A two-electrode electrochemical cell was designed to anodize Ti samples. The working cathode was a folded 100mm×50mm pure Ti ribbon. The treated Ti sample was used as anode. All parts were previously rinsed in ethanol to remove surface contamination. The cell was placed into a silica glass beaker containing 1% H₃PO₄ (phosphoric acid) solution as the electrolyte for anodic growth. Both electrodes were connected to a power supply during the anodizing process. A multi-function meter was also connected in the circuit to record the current.

![Schematic diagram of anodizing set-up.](image)

Fig. 3-2: Schematic diagram of anodizing set-up.

Ti samples were anodized by a quick galvanostatic voltage ramp-up (in seconds) which followed by a potentiostatic aging at the final voltage (10V or 30V) for varying lengths of time – 180s up to 86 ks (24 h). The dependence of voltage and current on time during anodization was schematically plotted in Fig.3-3. Based on the experimental observation, the leakage current density stabilized after about 4 ks and slightly dropped
after 86ks. The samples were then discharged and ready for further dielectric property measurements.

![Graphs showing voltage (U) and current (I) dependence on anodizing time (t).](image)

Fig. 3-3: Drawings of dependence of voltage ($U$) and current ($I$) on anodizing time ($t$). ($t_0$ is the time for voltage ramp-up)

3.7 Characterization

3.7.1 Leakage Current Measurement

Electric current can be transported through the dielectric layer electronically or by ion migration. In the present context, leakage occurs when a conductive path is available for electrons and they can flow across the dielectric layer.

Leakage current was recorded at both the anodizing voltage and at derated (reduced) voltages right after anodization. Voltage derating, by definition, is the reduction of a voltage rating to extend the lifetime of an electric device or to permit operation at a high ambient temperature. Typically, if a specimen was anodized at 30V, the derated voltages were defined at 3, 5, 10 and 15V, and if a specimen was anodized at 10V, the leakage current was measured at 3, 5, and 10V. The assumption is that further ion migration after anodization will only occur if the voltage exceeds the anodizing voltage,
so voltages lower than that mainly induce electronic current. Leakage current data were recorded after 120s when the current was relatively stabilized.

3.7.2 Capacitance Measurement

After leakage current measurements, capacitance was tested and calculated. A multi-function oscilloscope was used to record the capacitance at 6V and 120Hz AC.

3.7.3 X-Ray Diffractometry

XRD (X-ray diffractometry) can be used to determine the crystal structure at various states. XRD analysis was done by comparing the peak positions in the diffractogram of a sample with the standard XRD patterns from the Joint Committee on Powder Diffraction Standards database.

3.7.4 Electron Microscopy

Fig. 3-4: FEI Quanta (photo from SCSAM website)
Quanta 200 3D made by FEI is a versatile instrument operating with a dual-beam system (scanning focused ion beam and a scanning electron beam). In this project, SEM (scanning electron microscopy) is often used to provide information about sample’s surface topography and XEDS is commonly used for the chemical compositional characterization of a sample.

Fig. 3-5: (a) LIBRA 200FE made by Zeiss. (b) Tecnai F30 made by FEI. (photo from SCSAM website)

TEM (transmission electron microscopy) was carried out for selective cases to reveal nano-scale features of the metal–oxide interface. By examining the cross-sectional sample, conventional and high-resolution TEM were both used to provide basic bright-field and dark-field images of Ti oxide on Ti matrix and to elucidate the atomistic structure of the oxide. Electron diffraction patterns were acquired and analyzed to help determine the crystal structure of the Ti oxide through selected-area electron diffraction. XEDS and preliminary EELS (electron energy-loss spectrometry) also gave information about the chemical composition across the oxide layer.
3.7.5 X-ray Photoelectron Spectroscopy

XPS is a highly surface sensitive and quantitative spectroscopic technique that is used to study the materials about chemical composition and electronic state of the elements. In this work, the XPS spectra and depth profiles were obtained using PHI Versaprobe 5000 scanning x-ray photoelectron spectrometer on as-received Ti samples and N/O-infused ones with Ar⁺ sputter etching. The kinetic energy of Ar⁺ ions was set at 4keV, and (according to calibration with Ta₂O₅) the sputter rate was about 0.16nm/s.

![Fig. 3-6: PHI VersaProbe XPS Microprobe. (photo from SCSAM website)](image)

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4. TEM Sample Preparation Techniques

Selective etching refers to the differential attack on a specimen surface by a medium, typically a chemical, such that a specific component of the surface is removed significantly faster than the other. The etching depth can be controlled by the etching time and the known etch rate. The effectiveness of a selective etching method depends on the ratio of etch rates in the two materials. Selective etching techniques are very important in microfabrication and widely applied in glass and semiconductor industries.

4.1 Hydrofluoric Acid-Nitric Acid Solution Etching

Commercially pure Ti ribbon was employed for experiments to develop specimen technique for TEM. The ribbon was 5mm wide and about 200mm thick. TEM samples were prepared for two conditions: Ti with native oxide on the surface and Ti with anodized oxide formed on the surface. 3mm diameter discs were punched out for both types of specimens by using a mechanical disc punch. The edge was then covered with colorless lacquer to just expose the center region for wet-chemical etching. For anodized samples, the oxide was coated with a protective lacquer to prevent acid corrosion and to etch the desired region.

The specimen was dipped into a HF–HNO₃ solution (10% HF mixed with 10% HNO₃) and then rinsed with ethanol and water to remove acid residue. The effect of chemical etching on the sample was continuously monitored. The average time to etch through the Ti disc was estimated to be about 1.2ks. The etching was done intermittently with
longer initial immersion times of approx. 60 s to finally less than 10 s. The etching was done until a small hole was seen in the disc. After the sample was wet-chemically etched, the protective lacquer was dissolved in acetone.

![Image](image.png)

Fig. 4-1: Ti disc with anodic oxide after HF–HNO₃ Etching.

From Fig. 4-1, the anodic oxide remained after immersion in acid solution because of the protective lacquer layer and part of the disc was etched through and formed a 0.3 mm diameter hole. However, the edge of the hole was probably still more than 1 μm thick and this etching method failed to produce sufficiently electron transparent region.

4.2 Perchloric Acid Etching

A similar TEM sample preparation method was carried out with an 8% HClO₄-methanol solution. The Ti samples were prepared to have anodic oxide on one side and
fresh metal surface on the other to evaluate the etching effect. After etching in acid solution for 2ks, the Ti discs were not effectively etched on both sides at room temperature.

4.3 Hydrofluoric Acid and Sulfuric Acid Mixed Solution Etching

A methanol based solution with 10% sulfuric acid and 6% hydrofluoric acid was tested for thinning the sample discs. Both pure Ti samples and Ti oxide covered ones were studied for etching effect on Ti or Ti oxide. The results showed that surface oxide could be completely dissolved within minutes but no thinning effect was observed.

4.4 Bromine-Methanol Etching

The anodic Ti oxide film has been reported to be stripped off the substrate with 10% bromine-methanol solution at room temperature. The advantage of this method is acquiring the oxide film with minimal mechanical damage.

The nitrogen-and-oxygen infused Ti sample was cut into 3mm segments and immersed in 10% bromine-methanol solution. In this experiment, most of Ti samples with anodic oxide on both sides were etched for more than 2400s to collect enough peel off oxides. The oxide films were carefully “fished out” on a 3mm copper grid and rinsed further with methanol and distilled water to wash off the bromide residue.
4.5 Focused Ion Beam and Lift-out

The FIB (focused ion beam) technique uses a finely focused Ga ion beam for imaging and milling a specimen. It operates at low ion beam current for imaging and sputtering or milling is carried out at higher beam current. After its invention in the 1970s, FIB technique has been refined ever since. FIB is very useful for TEM sample preparation because it allows precisely choosing the thinning area. FIB also often used for semiconductor fabrication to either cutting unwanted parts or controlled deposition of materials to make new connections in an integrated circuit.

Fig. 4-2: Nova 200 Nanolab by FEI.

The Nova 200 Nanolab was used for precise FIB (focused ion beam) milling. Prior to ion milling, the nitrogen and oxygen diffused Ti sample was coated with 5nm Pd layer to increase the conductivity. Subsequently the sample was deposited with a protective Pt layer on a selective region to prevent sputtering by Ga ions. The Ga ion beam was used to make trenches by sputtering off material near the selected area till the remaining Ti
within that area was thin enough to be electron transparent under the 5 kv electron beam in the Nova.

Fig. 4-3: Nitrogen-and-oxygen treated Ti before lift-out.

A GIS needle was attached to affix the cut-off piece to a copper grid and the TEM sample was cleaned on both sides with a low energy (3-5kV) Ga ion beam before it was ready.

4.6 One-side Dimpling and Etching

For brittle materials, dimple grinding is a commonly used sample preparation method whereas the ductile metals may be dimpled by using some special techniques. The aim of dimple grinding is to thin the center of the disc while minimizing damage to the surface. 38
The pure Ti strips were mechanically polished to thin down to 100-150μm thickness and cut into 3mm discs with a Harris Micro Punch. The Ti disc was affixed onto the center of the dimpling stub with wax or super glue. Subsequently the disc was dimpled using a brass dimpling wheel. In the dimpling process, a 3μm abrasive diamond paste was used. The samples were dimpled down to 20-50μm thickness. Thinned samples were ultrasonically cleaned in ethanol for approximately 600s prior to etching. The Ti disc was dipped into a 5% HF mixed with 10% HNO₃ solution for final thinning in the center region.

Fig. 4-4: (a) dimple grinder. (b) Ti disc on the stub after one-side dimpling.
5. Results

5.1 Ti Surfaces

5.1.1 Microstructure of Ti Surfaces

As-received Ti wire surface is covered with a thin passive oxide formed by natural oxidation. In most cases in the present project, the as-received material was mechanically polished before further study to remove the surface oxide layer that was probably damaged or contaminated. The surface topography of the polished Ti sample was examined under SEM. Typical defects observed in the polished Ti surface are shown in Fig. 5-1.

Fig. 5-1: SEM micrographs of the polished Ti surface with SiC sandpaper.

Fig. 5-1 (a) shows the presence of polishing scratches or tracks left on the sample surface. The particles in the image are sandpaper particles that the specimen picked up
after polishing. Fig. 5-1 (b) shows more clearly crevices and pits on the surface. Those defects were most likely to have formed during the manufacturing process.

On chemical etching the specimen in an HF–HNO₃ solution (5% HF mixed with 10% HNO₃), the surface appeared to be rougher to the naked eye. The SEM images (Fig.5-2) show the surface topography after etching.

![SEM micrographs of chemically etched Ti surface.](image)

From Fig.5-2, it is clear that this solution effectively removed the initial surface of the as-received Ti specimen, but the etching failed to produce a smooth surface. As a result, the surface was cleaner but rougher after the etching.

A bright, shining metal surface was successfully obtained after the specimen was electropolished. Fig. 5-3, shows the surface of Ti specimen electropolished for 60s in an HF–H₂SO₄ electrolyte reported by Barker, and there were no visible cracks or particles on the specimen surface.
In comparison to mechanically polished surface shown in Fig. 5-1, the electropolished specimen had no crevices or particles on the surface, indicating that electropolishing successfully removed deep enough to get rid of the damaged surface layer and produce a surface free from impurities. In comparison to chemically etched surface shown in Fig. 5-2, the electropolished surface was microscopically smoother and visually brighter. Theoretically, the electropolishing method is more likely to produce a clean and flat surface free from stress.

5.1.2 Effect of the Surface Condition on the Leakage Current through a Dielectric Layer after Anodization

Leakage current densities through oxide layers grown by anodizing Ti samples with different surface morphologies were measured and plotted. Each sample was anodized in 1% $\text{H}_3\text{PO}_4$ electrolyte at 30V for 86ks (24h). All anodization and leakage current
density measurements were done at room temperature. The temperature in the oxide was expected to increase as a result of Joule heating during the anodizing process.

Fig. 5-4: Leakage current densities of anodic oxide on Ti under different surface conditions.

Fig. 5-4 shows leakage current density for different surface conditions. In general, the leakage current densities were too high for technical applications. But the leakage current density decreased when the surface impurities were removed by cleaning with an acid solution. The leakage current densities were lower if the specimens were etched with etchants that did not contain HF. The hydrogen absorption of Ti surfaces is likely to cause higher leakage current densities. The difference of leakage current densities between Ti chemically etched and electropolished with HF-based solution indicates that the surface roughness affects the properties of the anodic oxide film.
5.2 Infusion of Nitrogen and Oxygen

Fig.5-5: Leakage current density through TiO\textsubscript{2} layers formed on Ti samples (a) after polishing (b) after polishing and 6h N/O infusion

Fig.5-5 shows a significant decrease in leakage current density of Ti sample on measured voltages after infusion treatment. For infusion, the temperature and diffusion time are the two most important controllable parameters besides the surface condition. The effect of diffusion treatments varies depending on the different process parameters. The grain size, thickness of diffusion layer and diffusion concentration usually all relate to the treatment temperature and time.

5.2.1 Effect of Diffusion Temperature
The diffusion coefficient and diffusion depth for the designed treatment conditions were calculated and are listed in Table 5-1. The diffusion coefficient was calculated using equation (3) and diffusion depth \( d \) was calculated using \( d = 2\sqrt{Dt} \).

Table 5–1: Diffusion coefficients, \( D \), diffusion time, \( t \), and diffusion depth, \( d \), of nitrogen and oxygen in Ti.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Diffusing Element</th>
<th>Diffusion Coefficient ( D ) (cm(^2)/s)</th>
<th>Diffusion Time ( t ) (ks)</th>
<th>Diffusion Depth ( d ) (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>973 (α phase)</td>
<td>N</td>
<td>4.61x10(^{-12})</td>
<td>22</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>1.14x10(^{-11})</td>
<td>22</td>
<td>10</td>
</tr>
<tr>
<td>1073 (α phase)</td>
<td>N</td>
<td>2.18x10(^{-11})</td>
<td>22</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>9.76x10(^{-11})</td>
<td>22</td>
<td>29</td>
</tr>
<tr>
<td>1133 (α phase)</td>
<td>N</td>
<td>4.85x10(^{-11})</td>
<td>22</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>2.89x10(^{-10})</td>
<td>22</td>
<td>50</td>
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<td>7.91x10(^{-11})</td>
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<tr>
<td>1273 (β phase)</td>
<td>N</td>
<td>2.34x10(^{-10})</td>
<td>22</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>2.52x10(^{-9})</td>
<td>22</td>
<td>148</td>
</tr>
</tbody>
</table>

The theoretical diffusion depths of nitrogen and oxygen were much smaller than the sample thickness (0.52 mm).

Each Ti sample was subjected to a 22ks (6h) diffusion treatment followed by anodization in 1% \( \text{H}_3\text{PO}_4 \) electrolyte at 30V for 86ks (24h). After anodization, the leakage current values for each sample were recorded after 120s at 30V and reduced voltage of 3V, 5V, 10V, and 15V. The listed voltages in Fig. 5–6 are those at which leakage current densities were measured.
Fig. 5-6: Leakage current density of TiO₂ layers fabricated by anodizing of Ti samples after infusion of nitrogen and oxygen at different temperatures.

The leakage current curves in Fig. 5-6 show that the leakage current density correlates with the diffusion temperature. Also the leakage current densities increased with the increased applied voltage. The samples were treated under the same diffusion time and same anodization condition. In the tested temperature range of 700 to 860°C, the leakage current density decreased with the least leakage current at 860°C, because nitrogen and oxygen concentration near the surface increases with increased temperature (larger diffusion coefficient). Beyond 860°C, the leakage current started increasing with increasing temperature. And the reason is that solutes diffuse faster and deeper with further increased temperature, and due to limited nitrogen and oxygen in the retort, the solutes concentrations in the infused layer decrease.
The capacitance of each sample was measured right after the leakage current tests. The capacitance tests were carried out at a voltage of 6V and a frequency of 120Hz. The capacitance data with statistical errors has been plotted in Fig. 5-7.

![Capacitance of Ti samples after nitrogen-and-oxygen diffused at different temperatures.](image)

**Fig. 5-7**: Capacitance of Ti samples after nitrogen-and-oxygen diffused at different temperatures.

Fig. 5-7 shows that the capacitance of Ti samples had a similar correlation with diffusion temperatures as that of leakage current density. The recorded fluctuations in the capacitance data were the least at samples that were diffusion treated at 860°C. The fluctuation increased on either side of this temperature with increasing temperature difference.

5.2.2 Effect of Diffusion Time
The diffusion of nitrogen and oxygen into Ti was first investigated quantitatively by weight gain measurements of Ti samples. Prior to anodization, infused nitrogen and oxygen in Ti cause weight increase of a sample. All infusion-treated samples at 700°C for different time were weighed before and after infusion by using a digital analytical scale.

Fig. 5-8: Weight gain of Ti samples after different time diffusion at 973K.

The graph above shows the differences in the weight gain in Ti samples treated for 22ks (6h) and 86ks (24h) at the same temperature. The increased weight differences as a result of an increased time frame means that the longer treatment time, the more the amount of nitrogen and oxygen diffuse into Ti samples.
With fixed diffusion temperature, the Ti samples that were treated for 86ks (24h) exhibit lower leakage current density at most of the testing voltages than the ones that were treated for 22ks (6h). The increased treatment time allowed a deeper diffusion depth. The largely reduced leakages for Ti samples anodized at 10V and 15V in Fig. 5-9 show that the increased amount of nitrogen and oxygen in the Ti substrate as in the case of a 24h treatment is beneficial for reducing the leakage current densities.

5.2.3 Effect of Annealing Only

Experiments were designed to discriminate between effects from nitrogen and oxygen infusion and effects of annealing result from tempering that required by infusion of interstitial solutes. Fig. 5-10 shows that a Ti sample heated in high vacuum exhibited
higher leakage current density than the one heated with N₂ and O₂ at the same temperature for the same time period. This graph proves that the presence of nitrogen and oxygen does strong contribute to reduce the leakage current density.

![Graph showing leakage current densities](image)

**Fig. 5-10:** Leakage current densities of just heat-treated and diffusion-treated Ti.

5.2.4 O₂ inside the Retort

Ti is known to form a very stable oxide, and therefore the oxide is likely to form at very small partial O₂ pressure in the system. In this diffusion treatment, the amount of oxygen (0.00012 mol at the initial temperature, which is room temperature) trapped inside the retort was surely reacted with the Ti surface (sample, retort and getter) when the retort was heated in the furnace. Assuming the oxide was evenly distributed inside
the retort and formed a rutile structure, a total of $1.4 \times 10^{20}$ oxygen atoms would form a 0.3 μm thick TiO$_2$ on a total surface area of 66.8 cm$^2$.

Fig. 5-11: schematic structure of TiO$_2$ rutile. (red: O$^{2-}$, grey: Ti$^{4+}$)

5.2.5 N$_2$ inside the Retort

By adding saturation amount of reducing agents like, Ca or Mg, the amount of O$_2$ in the retort will be significantly decreased and N$_2$ will become the dominant element that diffuses into the specimen. However, the Ca or Mg residue on the specimen surface needs to be leached out after the heat treatment. Fig. 5-12 shows that the Ca concentration on the Ti surface can be up to 10 at% (+/-0.06) after the leaching process. For leaching out the Ca, the specimen was held in a 3% HNO$_3$ solution for 86ks (24h) after heated in the retort at 800 °C with 0.5g of Ca for 22ks (6h).
Fig. 5-12: SEM-XEDS result of the specimen leached out after treated at 1073K.

Preliminary results show that the leaching process could not completely remove the Ca. Then the Ca residue on the surface formed CaTiO$_3$ after anodization.$^{39}$

5.3 Anodization of Ti

5.3.1 Effect of Anodizing Voltage

The specimens were divided in 4 different groups and the Ti samples in each group were heat treated under the same conditions. After the diffusion treatment, all specimens were anodized firstly in 1% H$_3$PO$_4$ electrolyte for 4 ks at 10V or at 30V and measured separate leakage current densities later. The anodizing voltage was applied in full immediately instead of being ramped up. For each data point, the leakage current density data was recorded after applying the measuring voltage for 120s. Fig. 5-13 indicates that the increased anodizing voltage causes increased leakage current density.
Fig. 5-13: Leakage current density of anodic oxide at different voltages. (red: 30 V, black: 10 V)

N/O infused, 1173 K, 86 ks

N/O infused, 1273 K, 86 ks
5.3.2 Effect of Anodizing Time

The leakage current density data that were collected for testing the effect of anodizing time are plotted in Fig. 5-13. All pure Ti specimens were polished then anodized in 1% H₃PO₄ solution at 30V for different time. Generally the longer time the specimen was anodized for, the larger was the leakage current density that was observed. However, the leakage current density dropped after the specimen was anodized for 86ks. This was probably due to self-healing of the TiO₂ dielectric layer.

![Graph showing leakage current density for different anodizing times](image)

Fig.5-14: Leakage current density of anodic oxide for different anodizing times. (lines are only intended as visual needs.)
5.4 Microstructural Characterization of Anodic TiO$_2$

5.4.1 Surface topography

Fig. 5-15: SEM micrographs of the surface of the TiO$_2$ layer that formed by anodization on Ti substrates after different surface treatments. (a) on a Ti surface that was chemically etched (b) on a Ti surface that was electropolished. Anodization coditions: 1% H$_3$PO$_4$, 30V, 86ks.

Fig.5-15 shows SEM micrographs of the surface of the TiO$_2$ films that formed on Ti surface after different procedures of surface preparation (a) chemically etched and (b) electropolished before anodization. Both SEM micrographs show that the oxide layers on both surfaces are not as flat as the substrate surface but exhibit bubbles. The bubble size (1-2μm) in Fig.5-15 (a) is smaller and the oxide bubbles are more evenly distributed than those in Fig. 5-15 (b) (typical bubble size is 5-7 μm). The chemically etching gives a rougher surface of the Ti substrate than the electropolishing process and leads to the different oxide morphologies.
Fig. 5-16: SEM micrographs of the surface of the TiO$_2$ layer that formed by anodization on Ti substrates after different treatments (a) on as-received Ti (b) on a Ti surface that was treated at 1133 K for 22 ks. Anodization coditions: 1% H$_3$PO$_4$, 30V, 86ks.

Fig.5-16 (a) is the SEM micrograph of the anodic oxide grown on the as-received Ti substrate. In the image, the bubbles on the surface appear bright. The oxide surface in Fig. 5-16 (b) shows the bubbles decorate grain boundaries and a decreased density of the oxide bubbles which could be the consequence of the diffusion treatment. There are some line-shaped regions in Fig. 5-16 (b), indicating that the oxide on top is thicker, and those regions may be the grain boundaries where the oxide grows faster. In general, the anodic oxide grown on the infusion-treated at 1133K for 22ks substrate has a better continuity and may have better properties.

5.4.2 Chemical Composition of Substrate and Dielectric Layer
Fig. 5-17: (a) XPS depth profile of the as-received Ti substrate. (b) XPS depth profile of a Ti sample after the sample was treated at 1073K for 22ks.

In comparison to the depth profile of the nitrogen concentration in the as-received Ti wire, the nitrogen concentration in a treated sample has an error-function-type profile and shows an increased concentration near the surface. Fig. 5-17 gives the evidence that the diffusion treatment infuses nitrogen atoms into the Ti sample. The high level of oxygen in Fig. 5-17 (a) is a mistake of not thoroughly polishing the surface so the sputtered area has a thick oxygen-rich layer. By observing the Ti peak positions during the continuous sputtering, it assumed that there was probably no TiN or Ti$_2$N formation during the diffusion treatment because no Ti peak shifted after the initial sputtering, or the nitride phases were below the detector limit.
Fig. 5-18: TEM-XEDS results of the anodic oxide after treated at 1133K for 22ks.

Fig. 5-18 is a STEM image that is a Z-contrast image recorded with a HAADF detector capturing thermal-diffuse-scattered electron to get a mass-thickness contrast. In Fig. 5-18, the oxide layer appears darker than the substrate in the presence of oxygen (a lighter element). There is phosphorus in the TiO$_2$ and the XEDS results in Fig. 5-18 show that the phosphorus concentration decreases inwardly from oxide surface to
oxide/substrate interface. Since the phosphorus mostly came from the electrolyte, this result indicates that TiO₂ grows inward during anodization.

5.4.3 Microstructure of the Anodic TiO₂

XRD indicates nitrogen and oxygen diffusion into the surface of Ti. If Ti has nitrogen or oxygen in the solid solution, it exhibits an expansion of interatomic distances that can be observed as peak shift in x-ray diffractograms. Fig.5-19 shows the X-ray diffractogram obtained from an as-received Ti sample and a sample treated at 1133 K for 22ks. The scan is in the 2Θ range from 27° to 62°. The α-Ti peak positions are 2Θ=35.1° for [1010], 38.4° for (0002), 40.2° for (1011) and 53.0° for (1012). The scan displays that every α-Ti peak shifted from its normal position towards the lower diffraction angles, especially the Ti (0002) peak shifted from 38.4° to 37.7° and the Ti (1012) peak shifted from 53.0° to 52.3°. There is no detectable TiO₂ nor any Ti nitride (TiN, Ti₂N). The peak shifts indicate that the heat treatment expanded the Ti lattice parameter apparently without formation significant volume of Ti oxides or nitrides. However, the formation of oxides and nitrides could not be excluded because the volume faction could be below the detection limits of XRD.
Fig. 5-19: XRD result of a sample that was treated at 1133k for 22ks.

Fig.5-20 (b) is a TEM BF (bright-field) image of the anodic oxide grown on the Ti substrate without any heat treatment. In the image, the oxide is detached and some areas have holes and cracks. But the possibility that FIB milling created those holes or detached oxide structure could not be excluded. The growth direction of those cracks is vertical to the Ti substrate, and this uniform oxide is not a desired oxide structure for good dielectric properties. The image also shows the curtaining effect as a result of FIB milling.

The diffraction pattern of an oxide bubble recorded with a 5μm area-selecting aperture in Fig.5-20(c) is a series of concentric rings caused by different diffraction patterns from different grains superimposed. The average grain size of the bubble layer
is assumed to be 4 nm so the oxide is a nanocrystalline. The oxide has the crystal structure of anatase, which belongs to space group $I4_1/amd$.

Fig. 5-20: (a) SEM micrograph of a cross-sectional sample. (b) TEM BF image of the bubbles. (c) TEM diffraction pattern of the oxide bubbles.

Another continuous oxide layer is observed underneath the detached oxide. The thickness of this bottom layer in Fig.5-21(a) is about 40 nm and the oxide is relatively dense. The diffraction pattern (Fig.5-21(b)) shows a larger grain size than the loose oxide
and the rings are no longer continuous, so the grains in this region are probably not randomly orientated.

Fig. 5-21: (a) TEM BF image of the oxide/substrate interface. (b) Diffraction pattern of the bottom layer of oxide grown on as-received Ti substrate.

In comparison to Fig.5-21(a) and Fig.5-22(a), the TEM BF image of an anodic oxide grown on a substrate treated at 860°C for 22ks shows two continuous and uniform layers. The two layers have different crystal structures and different chemical compositions (the outer layer has a higher phosphorus concentration, according to the XEDS results in Fig.5-19). Both layers are a little thicker than the bottom layer in Fig.5-22(a) which is also dense and complete.
Fig. 5-22: (a) TEM BF image of the oxide grown on a sample after treated at 1133K for 22ks. (b) Diffraction pattern of the two layers of oxide.

In Fig.5-22(a), the outside layer (layer 1) of the oxide has no diffraction contrast in the BF image, so this layer may be amorphous. The inside layer (layer 2) in the image has bright spots so its structure could be crystalline. The range of the diameter of these crystals in layer 2 is roughly from 1nm to 10nm so this layer could be nanocrystalline. The diffraction pattern (Fig.5-22(b)) was recorded with 5μm area-selecting aperture and was contributed by both oxide layers. The layer 1 may contribute a diffuse diffraction pattern and the layer 2 may contribute the spots on the ring pattern which is a result of different diffraction patterns from those small grains superimposed.

Fig.5-23 is a STEM image of the same specimen in Fig.5-22 and it is a Z-contrast image. In this image, the interface of the two layers has larger grains so the interface appears to be darker. Both oxide layers are uniform and thickness of layer 2 (40nm) is larger than the layer 1(32nm).
Fig. 5-23: STEM image of the oxide grown on a sample after treated at 1133K for 22ks.

Fig. 5-24: (a) TEM BF image of the oxide grown on a treated substrate. (b) TEM DF image of the same region.

Fig.5-24(a) is a BF image and one DF (dark-field) image (Fig.5-24(b)) from the same area was recorded by selecting a spot in the diffraction pattern (Fig.5-22(b)). The DF
image gives further information that there is no diffraction contrast in layer 1 (amorphous oxide), and there are some bright spots in layer 2 (nanocrystals).

Fig.5-25: (a) HRTEM image of the 2 layers of oxide. (b) HRTEM image of the interface between two oxide layers.

Fig.5-25(a) is a HRTEM image of the same cross-section specimen that the anodic oxide grew after the specimen was diffusion treated at 860°C for 22ks. Fig.5-25(a) shows grains with different orientation in the nanocrystal layer (layer 2). Fig.5-25(b) is another HRTEM image that lattice fringes are seen so individual grain could be distinguished in the nanocrystal layer.

STEM images of a grain boundary in the Ti substrate and the top oxide were recorded. In Fig.5-26(a), the existence of the grain boundary did not affect the integrity of the oxide.
Fig. 5-26: (a) STEM image of a grain boundary in Ti matrix. (b) STEM image of the oxide grown on the grain boundary.

In Fig.5-26(b), the microstructure of oxide layers on top of the grain boundary remains the same. However, the thickness of each layer is different from the other regions. The amorphous layer becomes thicker while the nanocrystal layer becomes thinner. Therefore the total thickness of the oxide is roughly the same.

Fig.5-27(a) is a STEM image of a precipitate found underneath the oxide in one TEM thin foil. The precipitate is not likely an external particle based on the interface between it and the Ti substrate. By indexing the diffraction pattern (Fig.5-27(b)), the microstructure of this precipitate does not fit the regular phases of Ti oxides or Ti nitrides. The particle is more likely a Ti(OxN1-x), which is a TiN particle with oxygen solid solution.
Fig.5-27: (a) STEM image of a particle between oxide and matrix. (b) Diffraction pattern of the particle.

The presence of the particle changes the microstructure of the oxide on top of it. From Fig.5-27(a), the amorphous layer on top of this particle is thinner and the nanocrystal layer is thicker than the neighboring areas. As a result, the total oxide thickness is slightly decreased.
6. Discussion

6.1 Nitrogen Infusion of Titanium

6.1.1 Nitrogen Atoms in Ti Solid Solution

The diffusion treatment applied does not cause considerable volume fraction of Ti nitrides and Ti oxides to form but lead to infusion of nitrogen and oxygen in Ti solid solution. This can be explained that by sealing the specimen in the environment of air with a large getter surface of Ti (the ratio between Ti getter with retort and specimen is at least 15:1), it appears that most gas atoms is absorbed by the retort surface so the activity at the specimen surface is correspondingly small. This gas phase nitriding has achieved similar effect like kinetically-controlled nitridation: a large increase of interstitial solute concentration near the surface without the formation of the second phase. When the sample is infusion-treated, nitrogen atoms reside on the interstitial sites of Ti, and these gas atoms push Ti atoms apart. As a result, the lattice parameters of Ti expand as confirmed by XRD in Fig.5-19. For a sample that was treated at 1133 K for 22 ks, XRD results show the increased nitrogen surface concentration as the Ti peaks shifted to lower angle in the pattern with the largest expansion in the (0002) basal plane. Barker reported in 2010 that (0002) peaks show a larger shift to the left than others and a 0.3° peak shift of {1010} correlates to 12.5 at% of nitrogen in solid solution.\(^{33}\)
If there is a high concentration of interstitial atoms near the surface, the Ti atoms are farther apart than the average and subsequently, interstitial atoms jump more easily to neighboring sites, correspondingly to a lower activation energy for diffusion. Under this condition, the diffusivity of gas atoms (N, O) increases with increasing concentration of infused N/O atoms, similarly as the diffusivity of carbon increases with enhanced carbon diffusion at low temperature carburization of stainless steels.\textsuperscript{18}

Nitrogen atoms as solid solutes have a larger ability of expanding the Ti lattice parameters than oxygen atoms due to the larger size of nitrogen atoms. Nitrogen impedes oxygen intake of Ti during the diffusion process and subsequently interferes with the formation of TiO\textsubscript{2} during anodization. Chen reported that nitrogen doping affects TiO\textsubscript{2} surface restructuring and studied the effects of oxide defects on substitution of oxygen atoms with nitrogen atoms with nitrogen doping of TiO\textsubscript{2} anatase.\textsuperscript{40}

6.1.2 Effect of Infusion Temperature

Generally speaking, diffusion is dependent on the local concentration of the element (i.e., N, O). The diffusion coefficient is temperature-dependent. However, the final depth profile of the N or O concentration is not only affected by the diffusion coefficient. When the temperature is changed, the impingement rate of gas atoms at the surface would change as well as the kinetic energy and possible the dissociation rate. Firstly, the N\textsubscript{2} and O\textsubscript{2} are considered to be ideal gas. At different temperatures, the speed at which the individual gas atoms migrate in the presence of the concentration ingredient
changes, and also the rate at which the atoms bombard the certain area on the sample surface would be different within the fixed time period. The activity coefficient of the gas atoms is the activity divided by the atom fraction, and the activity depends on the chemical potential, which is a temperature dependent term. As a result, by changing the temperature, the thermodynamic factor changes so the concentration dependence of the diffusion coefficients varies.

Fig.6-1: Picture of an as-received Ti sample and Ti samples treated at different temperatures

In the temperature range of 700 to 860°C, the solubility of nitrogen in α-Ti increases with the largest solubility at 860°C, and the nitrogen concentration near the surface is expected to increase with increasing temperature. In the temperature range of 900 to 1000°C (beyond the phase transformation temperature), the solubility of nitrogen in β-Ti also increases with increasing temperature. In Fig.6-1, the Ti sample that was N/O-infused at 800°C was below the α—β phase transformation temperature. There are visible scratches made by polishing the surface before heat treatment. The Ti sample that was N/O-infused at 1000°C has no visible scratches but visible grains indicating α—
\(\beta - \alpha\) phase transformation and the sample is bent due to the phase transformation and grain growth. Apparently the different diffusion temperatures not only change the solubility of nitrogen and oxide in Ti according to the phase diagrams, but also provide different microstructures and roughness of the substrate that influence the growth of oxide.

![Fig.6-2: Picture of anodic TiO\(_2\) that formed by anodization on as-received Ti substrate and on Ti surfaces that was treated at different temperatures. Anodization coditions: 1\% H\(_3\)PO\(_4\), 30V, 4ks](image)

After the anodization, since the oxide layer is thin enough, the initial microstructure of the Ti substrate is still visible by optical microscopy. Fig.6-2 clearly shows the effect of different infusion temperatures on oxide growth. The oxides grown on the Ti substrates that were N/O-infused at 1173K and 1273K show different interference colors on different Ti grains. The Ti sample that was N/O-infused at 1073K is expected to have the highest nitrogen concentration in Ti solid solution, and the oxide that formed on this substrate are most uniform. At lowest temperature (973 K), the diffusivity of nitrogen in Ti may be too low to allow an adequate uptake of nitrogen atoms. At the highest
temperatures (1273 K), the limited amount of nitrogen and oxygen may have diffused deeper into the Ti substrate, leaving a more “flat” N/O concentration–depth profile.

The thickness of oxide films formed under a given anodizing voltage (30V) could be dependent on the orientation of the underlying Ti grain. Also the crystallographic orientations affect the migration rate of nitrogen and oxygen during infusion. The ability of forming uniform oxide is likely correlated to the nitrogen concentration in the substrate, which is affected by the diffusion temperature.

6.1.3 Effect of Treatment Time

The nitridation of Ti is a time-dependent diffusion process in which the nitrogen concentration at the surface increases with increasing time. The solubility of nitrogen in Ti is quite large in α-Ti and much smaller in β-Ti. Fig.5-8 shows that the weight gain of the samples slightly increased after a 4 times longer diffusion treatment time at 700°C. Also the XPS depth profile (Fig.5-17(b)) shows that the maximum nitrogen concentration is approximately 9at% at the surface of the nitrogen-enriched layer as a result of a 22 ks infusion treatment at 1073 K. In both cases, the nitrogen concentration may increase with an increasing treatment time due to the large solubility of nitrogen in α-Ti.

It is understandable that longer treatment time will infuse more atoms into the Ti matrix. But a much longer diffusion time will reduce the surface concentration of the N/O atoms since there are only a fixed number of gas molecules inside the Ti retort. If the diffusion time is infinite, the final surface concentration of N and O atoms should be
lower than the ones treated for 86ks because the gas atoms tend to be evenly distributed in the whole sample instead of a shallow surface layer.

It is known that once the Ti nitrides or Ti oxides have formed, they would not redissolve.

6.2 Oxide Growth Mechanism

While the oxide layer is growing, it is also simultaneously dissolving. And it can be assumed that the dissolution rate is just given by the temperature and chemical composition of the electrolyte and is not impact by further parameters that affect the oxide growth rate. Initially, the rapid voltage ramp-up generates a large electric field strength for electric-field-driven diffusional ion transport and the ion transport is fast with a small diffusion distance, which gives a much larger oxide growth rate than the rate of oxide dissolving.

Fig.6-3: Schematic of two possible oxide growth mechanisms. (Upper oxide: amorphous; Lower oxide: crystalline)
There are two possible oxide growth directions and they can act separately or simultaneously: oxide may grow inwardly by migrating O$_2^-$ into the oxide/Ti interface to form new oxide, or the oxide may grow outwardly if the Ti ions migrate through the oxide. The two mechanisms are sketched in Fig.6-3. Also, the growth of anodic TiO$_2$ may involve the simultaneous migrations of anion and cations.$^{14}$ Under the combined influence of a large electric field strength and infused nitrogen, which expands the lattice parameters and lowers the energy barrier for diffusion, the rapid growth of the initial oxide could have an amorphous structure. It is known that under high driving forces and low mobility, the material tend to solidify in amorphous form rather than crystalline form, because these is not enough time for atoms to sit in the correct positions in a crystalline structure so they remain amorphous. The direction of growth may also depend on the microstructure. For instance, the grain boundary of oxide may be good channels for rapid inward diffusion of oxygen.

In the first step of anodization (galvanostatic mode), there is an initial voltage surge because of the native TiO$_2$. Then the voltage ramp-up at a constant rate and the thickness of oxide is proportional to the applied voltage. During the galvanostatic step, the amorphous-crystalline transformation would probably happen when the voltage reaches at least 10V and the pre-cursor nuclei in the native TiO$_2$ may cause the crystals (anatase structure) to form in the metal/oxide interface.$^{14}$ The amorphous-crystalline transformation would decrease the oxide growth rate and cause a change in resistivity and voltage ramp-up rate. After the voltage reaches the predetermined forming voltage, the oxide continues to grow in the following potentiostatic aging step. When the oxide
grows thicker, the ion transport slows down with decreased electric field strength and increased film thickness as the diffusion path. If the oxide reaches a critical thickness, the growth rate has dropped to a level that equals the dissolution rate, and from then on the oxide thickness does not change anymore even though the oxide is still being dissolved and growth rate is such that the dissolution rate is exactly compensate.

The presence of nitrogen could interfere with formation of crystalline oxide. Nitrogen solutes could not move sufficiently during the formation of TiO$_2$ by anodization, and subsequently nitrogen inhibits the crystalline structure to be formed. XPS shows preliminary results of this effect. Since the nitrogen diffusion depth was measured by XPS and it shows more than 25nm in thickness of nitrogen-infused layer after the specimen was treated at 1073K for 22ks, which is close to the thickness of amorphous oxide formed on Ti substrate that was treated at 1133K for 22ks. After this nitrogen-rich layer was used up during anodization, the crystalline oxide can form with nitrogen-free TiO$_2$. The anodic TiO$_2$ microstructure model is illustrated in Fig. 6-4 to show the effect of nitrogen in Ti solid solution on the formation of anodic oxide.
According to the literature, an amorphous region forms at the oxide/electrolyte interface by outward diffusing of Ti\textsuperscript{4+}.\textsuperscript{14,16,17} If the crystalline oxide grows inward, the O\textsuperscript{2−} subsequently migrates through the amorphous layer to form TiO\textsubscript{2} at metal/oxide interface. With increasing oxide thickness, the decreasing driving force and longer diffusion distance make the O\textsuperscript{2−} more difficult to travel through, and hence the oxide grows slow down. The slower growth rate of the oxide gives atoms sufficient time to form an oxide with an ordered structure, i.e., crystalline oxide. As a result, a nanocrystalline oxide layer forms underneath the amorphous oxide layer. Eventually, the oxide near the metal—oxide interface grows very slowly but the grain size is small due to lack of growth time.

The microstructure and defect population of TiO\textsubscript{2} by different growth rates have significant influence on the functional properties of the dielectric, and most experimental studies have stated that increasing the growth rate of the oxides yields
more insulating oxide films. Therefore, the formation of an amorphous oxide layer is beneficial with regard to the leakage current density, indicating that extended structural defects in crystalline TiO₂ are responsible for leakage current.

6.3 Leakage Current Mechanisms

There are two main properties of the dielectric that affect the leakage current density at a given voltage: the thickness of the dielectric oxide and the atomistic structure of the dielectric oxide.

6.3.1 Applied Voltage

The leakage current density is voltage-dependent and usually increases with increasing applied voltage. Because increasing the voltage causes a larger electric field strength \( E = \frac{U}{d} \), where \( U \) is applied voltage and \( d \) is the dielectric thickness, which gives a larger driving force to push electrons through the dielectric layer, a high leakage current density would subsequently be observed. And the electric field strength determines which type of oxide structures to form.
Fig.6-5: Picture of anodic TiO$_2$ that formed by anodization at different anodizing voltages

The specimens in Fig.6-5 were infusion-treated under the same conditions and anodized in the 1% H$_3$PO$_4$ for 4 ks but at different voltages (10V or 30V). The leakage current density data in Fig.5-13 indicates that a thicker anodic oxide made at 30V exhibits lower resistivity than a thinner oxide made at 10V at the same testing voltages. Usually, a thicker oxide made by potentiostatic annealing with increased final voltage should have a smaller leakage current density because the increased thickness should reduce the average electric field strength, assuming the oxides of both samples have similar structure. A possible explanation for Fig.5-12 is that when a higher formation voltage (30 V) is applied, the crystalline part of oxide layer grows thicker. Therefore, an increased level of growth stresses may arise and damage the initially formed amorphous layer to increase its conductivity, e.g. by cracking.$^{41}$ Moreover, higher formation voltage makes the crystalline part of the layer grow faster and – therefore – less dense and with higher concentration of structural defects. Furthermore, it is possible that with a higher voltage, the side reactions during anodization induce more impurities into the anodic
oxide. As a result, the anodic oxide made at 30 V most likely has a higher electric conductivity than that obtained with a formation voltage of 10 V.

6.3.2 Crystal Defects and Impurities

Extended structural defects in the Ti substrate may be caused by manufacture process or mechanical polishing. Those defects in the Ti substrate could propagate into defects in the oxide generated by anodization. And those defects certainly interfere with the function of the dielectric layer.

Grain boundaries are considered to be fast paths for ion diffusion. Along the grain boundaries and certain crystalline defects such as dislocations there is more open space, thereby allowing for lower activation energy for diffusion. During the anodization, the ions diffuse faster through the grain boundaries so the oxide growth rate on top of the grain boundaries is larger than the neighboring area. Subsequently the amorphous layer appears to be thicker while the nanocrystal layer becomes thinner on top of the grain boundary in Fig5-26(b).

The amorphous structure of TiO₂ as a dielectric material eliminates the dislocations and grain boundaries so it is homogeneous at the atomic level. Plus this type of dielectric can self-repair in oxidizing electrolyte up to a certain thicknesses.

Usually, surface impurities and the damaged layer on the Ti substrate generated by polishing can be effectively removed by wet-chemically etching or electropolishing. Fig. 5-4 shows that leakage currents decreased when the surface impurities were removed
by cleaning with an acid solution. The leakage current densities of the dielectrics grown on Ti substrates under different surface conditions show no significant leakage current decrease after electropolishing process even the electropolishing successfully reduce the surface roughness and release the stress. The reason for the high leakage current densities is probably the absorption of hydrogen in the process. Hydrogen, as one of common impurities in Ti matrix, is known for giving rise to leakage current as a charge carrier. In this project, the hydrogen absorption happens either in electrochemical processing like electropolishing or during the anodization. The effects of hydrogen in TiO₂ would probably be that the bonding of atomic hydrogen in oxide and hydrogen-assisted oxide damage, similarly as Afanas'ev reported about hydrogen-related leakage current in SiO₂. The temperature of the anodic oxide was significantly increased by the current density when the specimen was anodized in the room temperature, leading to more hydrogen pick-up. The hydrogen concentration in the Ti matrix can be effectively reduced by high temperature vacuum annealing.

6.3.3 Residual Stress after N/O Infusion

After the diffusion treatment, the specimen is expected to be in compression at the surface due to the expansion of lattice parameters. And further into the specimen, where the concentration of nitrogen in Ti solid solution becomes quite small, the residual stress should decrease and, eventually, the core of sample should be in tension to balance the compressive stress at the surface. However, since the core is thick compared to the infused layer, the debilitative stress level in the core is actually
negligible. The compressive stress in the surface layer may increase the chemical potential of nitrogen.

Furthermore, the compressive stress caused by Ti lattice parameter expansion helps release some of the tensile stress during the oxidation reaction and protect the integrity of oxide film, lowering the chances of oxide peel-off.
Conclusion

This project examined the relationship among the diffusion of the interstitial solutes (N, O) into a base material (Ti), corresponding decreases in leakage current density and capacitance of the anodic Ti oxide.

Nitrogen and oxygen infusion can be controlled by varying the diffusion treatment temperature and treatment time. The XRD and XPS results show evidence that the diffusion treatment can successfully infuses nitrogen and oxygen to obtain a solid solution that is practically free of Ti nitrides and Ti oxides. The XPS depth profile shows that a 22ks long diffusion treatment at 1073K increases at least 7at% nitrogen concentration near the specimen surface and gives a conservatively estimated 25nm diffusion depth. The presence of nitrogen and oxygen may interfere with the crystal formation of crystalline TiO₂. And it is commonly known that the solutes (nitrogen and oxygen) inhibit the crystallization by having a large size mismatch of solutes, leading to an amorphous structure.

The mechanism that causes the leakage is discussed and is assumed to be the consequences of crystalline structure, mechanical stress and possible impurities in the Ti dielectrics.

A Ti-based electrolytic capacitor may lose its capacitance and degrade when it has large leakage current goes through the dielectric. The infusion treatment of nitrogen
may help extend the life cycle of the capacitor since the method can produce better uniform metal oxide with reduced the leakage current density.

The observation of the double-layer structure of dielectric oxide gives evidence of oxide growth mechanism, which is inward migration of O\(^{2-}\) for crystalline TiO\(_2\) rather than outward migration of Ti\(^{4+}\).

Overall, the presence of nitrogen in Ti solid solution interferes with forming crystalline TiO\(_2\), and therefore can be useful for generate an amorphous TiO\(_2\), which has better dielectric properties. Similar properties may apply for capacitors made by anodization of other metals. The results of the current project have really given important insights to controlling and improving the dielectric properties of TiO\(_2\) formed by anodization through alloying Ti substrate prior to anodization.
Future Work

The experiments designed and carried out in this project were focused on investigating whether infusion of nitrogen and oxygen can alter the dielectric properties of TiO$_2$ layer resulting of anodization. However, there are many other important parameters of dielectric properties, such as energy density and time constant, have not been evaluated.

The present studying of nitriding may inspire further research to assess the effect of other possible additives that could improve the dielectric properties of TiO$_2$. Also the method of gas-phase surface alloying of Ti with nitrogen and oxygen as interstitial solutes should be possible to improve the surface properties of a large variety of Ti-base alloys or other valve metals with different interstitial solutes (carbon, nitrogen, oxygen, hydrogen).

The nitrogen concentration and thickness of diffusion layer are both comparatively small compared to the results reported by kinetically-controlled nitridation of Ti and Ti alloys. The effect of much larger depth of nitrogen diffusion and high concentration of solutes should be evaluated to improve the function of nitrogen in Ti solid solution.

An experiment of stopping the process at different anodization stages and analyzing the microscopic structure of the anodic oxide would be useful to improve the understanding how the change of voltage or current in galvanostatic mode and potentiostatic mode affect the oxide morphology and dielectric properties.
Some results recorded in the project that are preliminary or limited by the quality of the specimen preparation. For example, the EELS preliminary results show the O edge and N edge beneath the oxide on the Ti substrate of a diffusion-treated specimen. Unfortunately, the quality of the TEM foil was not good enough for further analytical studies. With a much thinner and cleaner TEM specimen, EELS will be useful for quantifying the oxygen and nitrogen concentration in the specimen.

Fig. 7-1: (a) STEM image of a cross-sectional anodic oxide grown on infusion-treated Ti substrate. (b) O edge in EELS spectrogram. (c) N edge in EELS spectrogram.
References:


