TITANIUM OXIDE NANOWIRE GROWTH BY OXIDATION UNDER A LIMITED SUPPLY OF OXYGEN: PROCESSING AND CHARACTERIZATION

DISSERTATION

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ABSTRACT

Instead of using expensive and complex methods to produce 1D structures, a simple direct oxidation method has been developed to produce either pure TiO₂ nanowire or heterogeneous nanowires under a limited supply of oxygen. The dimension of the nanofibers ranged from 30 to 60 nm in diameter and their length were between 500 nm to several μm depending on Ti alloy samples. Experimental parameters such as flow rate, heat treatment temperature, and gas constituent have effects on the surface morphology of the samples. Based on studies under various conditions, pure TiO₂ nanowires were only grown on pure Ti samples at the heat treatment temperature of 600 °C with an Ar flow rate of 200 ml/min. As the heat treatment temperature increased, well faceted crystals were formed and connected to each other to form a continuous oxide scale. As the flow rate increased, the formation of nanowires were hindered and an oxide layer was formed rather than the formation of nanowires. The phase of nanowires was determined to be rutile based on SAED pattern from TEM analyses.

For Ti alloy samples, the growth of nanowires was accelerated in terms of the density and length. The effects of the heat treatment temperature on the surface morphology were similar to those of pure Ti samples. However, the effect of the flow
rate was not prominent as those of pure Ti samples. Consequently, the growth processing window for Ti alloys is larger than that of pure Ti samples with respect to the flow rate. The phase characterization of nanowires by XRD and TEM analyses indicated that the inner rutile core was covered by an Al rich outer layer.

While the growth mechanism for nanowire formation is not well understood, it is established that the growth occurs at the tip and that the rate limiting step is the transport of oxygen through the gas boundary layer. Additionally, 1D growth implies surface reaction anisotropy that disappears at high temperature promoting oxide cale growth. The Based on experimental observations, a four-stage mechanism is proposed as a function of time. In stage I, a cracked oxide scale grows followed by the formation of bumps in stage II that act as nucleation sites for nanowires. In stage III, nanowires continue to grow along with nucleation and growth of new nanowires leading to the increase in density. In stage IV, the density of nanowires is so large that the accessibility of oxygen to the base becomes difficult and nanowires continue to grow at the tip.
Dedicated to
Craig, Kayla and Heeseong
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CHAPTER 1

INTRODUCTION

It is believed that nanostructured materials such as nanobelts, nanowires, and nanoparticles can show peculiar properties at nanoscale. The reasons for these properties may be due to their dimensionality [1-6], enhanced surface area [7-12], and electronic states [13-17]. Therefore the fields related to nanotechnology, which includes fabrication and characterization of nanostructured materials, have drawn much attention and required fundamental insight to understand these unique properties. One of the most exciting possibilities is to use these nanostructured materials as building parts for components such as memory devices [17-26], chemical sensors [6, 8, 9, 11, 12], and micro- and nanoelectromechanical devices [27-29] (MEMS and NEMS).

Research on 1-D nanostructured oxides has been intensified as of late due to their intrinsic properties such as electrical transport [16, 30], photoelectronic [31-37], and mechanical properties [38-41] compared to those of their traditionally fabricated bulk counterparts. The applications of these nanostructured oxides include biological [42-45] and chemical gas sensors [46-51], photocatalysis [52-63], electronic [17, 18, 64-67] and optoelectronic devices [32, 68, 69]. Many research groups have developed a large number of fabrication techniques to obtain 1-D nanostructured oxides and their properties
have been reported. This chapter briefly introduces and discusses many of these techniques.

### 1.1 Fabrication of 1-D nanostructured oxides

Many fabrication techniques for nanostructured materials, especially 1-D nanostructures, have been developed to make various oxides such as ZnO [70, 71], Ga$_2$O$_3$ [72-75], TiO$_2$ [18, 56, 58, 76-80], SnO$_2$ [71, 81-84], CuO$_2$ [85-90], and SiO$_2$ [91-94]. The fabrication techniques can be divided into two methods, top-down and bottom-up by considering where the growth or fabrication of 1-D nanostructures starts.

In the top-down approach, nanostructures including nanowires or nanorods can be easily fabricated by the techniques commonly used to produce microelectronic devices [23, 78, 95]. With the aid of electron beam lithography and other lithography techniques, nanostructures with well controlled diameters can be obtained. The fabrication of single crystal TiO$_2$ nanowires on SiO$_2$ mesa by using such a technique was reported by Francioso et al. [78]. The fabricated nanowire is shown in Figure 1.1C. The width of the nanowire was 90 nm. Martinez et al. [23] also reported a transistor using multiple Si nanowires using Atomic Force Microscopy (AFM) along with Reactive Ion Etching (RIE) and patterning techniques. The advantage of these techniques is that the accurate control of diameter and length of nanowires can be easily established. However, the technique requires very expensive equipment like electron beam lithography and high vacuum deposition systems. Additionally, a restriction of materials for nanowires exists due to the possibility of etching and the diameter of nanowires is limited by the resolution
of lithography. The complex procedures and many steps as described in Figure 1.1A and 1.2 also hinder wide spread deployment of this technique as a means of producing 1-D nanostructured materials for commercial applications.

In contrast to the top-down approach, nanoscale building blocks can be directly fabricated by chemical synthesis from substrates in the bottom-up approach [95]. There would be no limitation on the diameter of nanowires or nanorods from the bottom-up approach as is seen in the top-down approach. There are many fabrication techniques which employ this approach including: VLS (Vapor-Liquid-Solid) [96-98], VS (Vapor-Solid) [74, 99], SLS (Solid-Liquid-Solid) [100-102], SoLS (SOlution-Liquid-Solid) [103-108], template assisted growths, and metal oxidation methods [109-114]. Among them, the most well established synthesis method is the VLS (Vapor-Liquid-Solid).

1.1.1 1-D nanostructured oxides by VLS and SLS growth

In order to make 1-D nanostructures such as nanowires, nanobelts, and nanoribbons, there needs to be a way to confine the growth direction of nanostructure to one dimension either physically or chemically. In VLS method, liquid metal droplets which are formed by the reaction between a source material for the nanostructures and a metal catalyst act as chemically favorable sites for adsorption of the source material for 1-D nanostructures [115]. The mechanism for the VLS will be discussed in Chapter 2.

For producing vapor gas for the VLS technique several methods such as thermal evaporation [116], carbothermal evaporation [117, 118], laser ablation [115] and metal organic precursors as gas sources [119-124] have been used. By this fabrication method,
several oxide nanostructures such as nanoribbons and nanowires have been reported [70, 79, 125].

The fabrication of Si nanowires by using a laser ablation method was reported [115]. In this method, a Si$_{0.9}$Fe$_{0.1}$ target at temperatures greater than 1200 °C was used to produce a vapor of Si and Fe that rapidly condense into Si-rich liquid Si-Fe nanoclusters and when a supersaturation of the nanoclusters is achieved, the Si phase precipitates and grows as nanowires or nanobelts. Some typical images of Si nanowires with Fe metal cap are represented in Figure 1.3A [115]. The length and diameter of nanowires were over 1 and 0.01 μm, respectively. One of the interesting features of the nanowires is the existence of amorphous SiO$_2$ layer covering the inner Si core as show in Figure 1.3B. Figure 1.3C shows that the growth direction of the nanowire is [111]. Using a mixture of ZnO and SnO$_2$ powders in a weight ratio of 1:1 as the source material, a complex ZnO nanostructure was fabricated [70]. Figure 1.4A shows a low magnification image of the as-synthesized products with a uniform feature consisting of sets of central axial nanowires surrounded by radially oriented tadpole-like nanostructures [70]. Caps are observed on tips of ZnO nanostructures as shown in Figure 1.4B. The growth direction of a branched nanostructure is [1000] and the SAED (selected area electron diffraction) pattern from TEM analysis indicates that the tadpole-like nanostructure and the central nanowires are ZnO. Electron Dispersive Spectroscopy (EDS) shows that the chemical composition of the cap at the tip is Sn. The presence of Sn metal cap means that Sn acts as a metal catalyst for the fabrication of ZnO nanostructures. According to Yang et al. [126], ZnO nanowires were also fabricated on Au-coated Si-substrates by a carbothermal
method under a constant flow of Ar for 5-30 min at 900 - 925 °C. **Figure 1.5** shows images of a nanowire of ZnO. An Au cap is observed on the tip of a ZnO nanowire and the diameter of the nanowire is around 100 nm. The lattice image shows the growth of the nanowire along <0001> direction.

The fabrication of TiO$_2$ nanowires by the VLS method has also been reported in the literature [79]. Wu et al. [127] reported the growth of TiO$_2$ nanowires by using Au seeds formed during the heat treatment. They believe the growth of TiO$_2$ nanowires by the VLS while some of the nanowires do not show the characteristic caps on the tips in **Figure 1.6**. The growth direction and phase of the nanowires are [110] and rutile, respectively. The fabrication of TiO$_2$ nanowires was also performed using thermally evaporated Ti and Au deposited on sapphire and quartz substrates, which was reported by Lee et al. [79]. It is worth noting that Ti buffer layers for the growth of nanowires were used to supplement Ti vapor to the Au catalysts. From HRTEM (High Resolution Transmission Electron Microscopy) results, there is a twin along the tip of the nanowires grown on a sapphire substrate as shown in **Figure 1.7**. They argue that the growth of TiO$_2$ nanowires occurs by the existence of twin. In addition, no cap is observed on the tip of a nanowire.

Zheng et al. [100] reported ultra long and highly oriented Si oxide nanowires from liquid alloys along with GaN nanowires. **Figure 1.8** shows the image of nanowires. They argued that the growth of Si oxide nanowires was due to the diffusion of Si from a bulk Si wafer to the surface of a drop of Ga liquid and then the diffused Si interacted with water vapor to form silicon oxide nanowires. Because there were no vapor species of Si,
this method was called Solid-Liquid-Solid (SLS) method. Yu et al. [101] and Lee et al. [102] also reported the growth of Si nanowires by this method. Yu et al. used Ni coated Si wafer as a template for the growth of silicon nanowires and \( \text{Ni}_2\text{Si} \) droplets were formed and Si diffused through liquid alloy droplets, resulting in amorphous silicon nanowires. As shown in Figure 1.9, Lee et al. also used Ni as an agent to form liquid droplets and they concluded that the diameter of nanowires was not related to the size of liquid droplet governed by a reaction temperature.

### 1.1.2 1-D nanostructured oxides by VS method

While a metal catalyst is used to confine 1-D nanostructure growth in the VLS method, the VS method only consists of the evaporation of a source material and then subsequent condensation of the vaporized source on a substrate which is usually located at a lower temperature zone. Table 1.1 summarizes the synthesis conditions for various metal oxides with their characteristic morphology [128]. It is worth noting that the VS growth requires high temperature to generate enough vapor source material. There is controversy about the mechanism used to explain the formation of 1-D structure by the VS method. It is believed that some defect structures like screw dislocations and twins may play a key role in the formation of these abnormal structures. However, there is no physical evidence of the relationship between defects and the formation of 1-D nanostructures grown by this method. ZnO nanowires have been produced using this method [129]. Ultra long ZnO nanobelts were obtained by thermal evaporation of ZnO powders (purity: 99.99 %; melting point: 1975 °C) at 1400 °C. No metal cap was observed at the ends of ZnO nanobelts, which indicates that the growth of the nanobelts...
was not achieved by the aid of a metal catalyst. Each nanobelt has a uniform width along its whole length, and the typical width of the nanobelts ranges from 50 to 300 nm. Their unique geometrical shape is shown in Figure 1.10. Other oxide nanobelts like SnO$_2$ [129-132], In$_2$O$_3$ [129, 133], and CdO [129] grown by the VS method were also reported. There are only a few papers about the fabrication of 1-D TiO$_2$ nanostructures using this method because of a low vapor pressure of Ti and TiO$_2$. For the fabrication of TiO$_2$ nanowires by the VS mechanism, Wu et al. reported a two step thermal evaporation process with a radio frequency heater (350 kHz) used to generate enough Ti vapor pressure [134]. In the first step, they formed high surface energy TiO$_2$ seeds on an alumina substrate and then the substrate with TiO$_2$ seeds was placed in a low temperature zone while supplying Ti vapor species generated from a high temperature zone. The growth of nanowires was preceded by the transport of Ti vapor species which condensed on the seeds and grew as nanowires. The diameters of these nanowires were in the range 50 – 100 nm and the length of nanowires were in the range 1 – 2 μm. They grew along the [110] orientation as illustrated by the HRTEM images in Figure 1.11.

1.1.3 1-D nanostructured oxides by SoLS method

Most of the 1-D nanostructure growth using catalyst has been performed in the vapor phase deposition methods through the VLS method. Gibbons et al. [135] developed a process called Solution-Liquid-Solid (SoLS) method. Dingman et al [108]. reported the growth of InN nanowires by using this method. Nanometer size metal droplets formed at 203 °C acts as catalytic sites for the formation of nanowires and a schematic processing
diagram for the growth is presented in Figure 1.12. The precursor for this process is either $i$Pr$_2$InN$_3$ or $t$Bu$_2$InN$_3$ as solution phase. InN amorphous or crystalline nanowires form resulting from the reactions between a reductant $1$, 1-dimethylhydrazine, $H_2N$NNMe$_2$ and either $i$Pr$_2$InN$_3$ or $t$Bu$_2$InN$_3$. Heitsch et al. [103] announced the growth of Si nanowires by this method. They used trisilane (Si$_3$H$_8$) as a reactant in octacosane (C$_{28}$H$_{58}$) or squalane (C$_{30}$H$_{62}$) with Au or Bi as a catalyst. Au forms an eutectic liquid alloy with Si at 363 °C and it interacts with trisilane and then form Si nanowires. There are no vapor species because all the solution (trisilane, octacosane and squalane) have high boiling temperature over 420 °C. Dong et al. reported the growth of ZnSe nanowires by using Bi as a catalyst [105].

1.1.4 1-D nanostructured oxides by template assisted growth

There is a simple technique called template assisted growth which is used to suppress the growth of 1-D nanostructures physically in an anodized alumina membrane (AAM), carbon nanotube, or polymer membrane. In the template assisted growth technique, the pores in the templates are filled by sol-gel [80, 136-140], electrochemical [141, 142], or chemical vapor deposition (CVD) methods [143-146]. The anodization of aluminum metal in acidic solution results in porous AAM [147-152]. Figure 1.13 shows the resulting regular hexagonal pore structures and pore densities as high as $10^{11}$ pores cm$^{-2}$ can be achieved [151, 152]. The pores in the membrane are very straight along the direction of the thickness of the membrane, which indicates that the pores in the membrane are isolated. Microporous and nanoporous polymer membranes can also be used as the template for the growth of 1-D nanostructure. The fabrication of the pores in polymer
membranes is obtained by bombarding a non-porous sheet of polymers with nuclear fission fragments to create a damage track in the material. This track is then chemically etched to produce pores [153]. A broad range of pore diameters is available and the densities of pores can be as high as $10^{11}$ pores cm$^{-2}$.

To fill the pores in a membrane, sol-gel technique can be used to prepare inorganic materials. Martin’s group is the first to conduct sol-gel synthesis within the pores of the AAM template to create both fibrils and tubules of the desired material, using a simple immersion method. First, the AAO membrane is immersed into a sol for a given time depositing the sol on the pore walls. After thermal treatment, either a nanotube or nanofibril is formed within the pores. By this method, nanowires and nanotubes of TiO$_2$ [80, 136-138], SiO$_2$ [139], In$_2$O$_3$ [140], MnO$_2$ [136], WO$_3$ [136], Fe$_2$O$_3$ [154], and SnO$_2$ [155] have been synthesized.

According to Martin et al. [136], tubules and fibrils of TiO$_2$ were obtained by using titanium isopropoxide as the precursor for the sol-gel preparation. After preparing the sol-gel solution, the AAM with 200 nm diameters was dipped into the sol-gel solution for various times and then the membrane was dried in air for 30 min. The membrane was subsequently heated to 400 °C for 24 hours in air. Figure 1.14 shows the tubules and fibrils of TiO$_2$ after various immersion time periods. The method of template assisted growth has some potential limitations. For example, the filling of the pores would be difficult for the sol with higher concentrations because the capillary force is the only driving force to fill out the pores but using too low a concentration results in the cracking and shrinkage of nanostructures. Miao et al. [156] reported that single crystalline TiO$_2$
nanowires can be produced by using electrochemically induced sol gel methods to overcome these problems. A schematic diagram of electrochemically induced sol gel method is presented in Figure 1.15. At first, the cathodic reduction causes the formation of hydroxyl ions, thus resulting in the increase in the local pH at the electrode surface. Therefore, the electrode surface promotes the titanium oxyhydroxide gel formation in the pores of the template. The TiO$_2$ nanowire arrays are finally obtained from subsequent heat treatment and the removal of the template by chemical etching. This electrochemically induced sol gel method can prevent the shrinkage problem caused by the direct growth of nanowires from the AAO template.

### 1.1.5 Other fabrication methods for 1-D nanostructured oxides

Other techniques such as anodization and electrospinning can be used to fabricate 1-D nanostructured oxides [157-166]. Yoriya et al. [162] reported the fabrication of vertically oriented TiO$_2$ nanotube arrays using an electrolyte of dimethyl sulfoxide (DMSO) containing either hydrofluoric acid (HF), potassium fluoride (KF), or ammonium fluoride (NH$_4$F) with various anodic oxidation variables. Figure 1.16 shows the morphology change of the surface depending on voltage. Using an anodization potential of 60 V with an electrolyte of 2% HF in DMSO, 70 h duration, nanotubes are achieved having a length of 101 μm, inner diameter of 150 nm, and wall thickness of 15 nm.

Electrospinning has been intensively investigated to produce nanowires because of its simplicity and functionality over a variety of materials [77, 167-169]. The technique uses a polymer solution or melt which is injected through a small nozzle. A
strong electric field (a few kV/cm) is applied to the nozzle. The liquid droplet from the nozzle contains the buildup of electrostatic charges on the surface and the formation of a wire is obtained by stretching of this liquid droplet. Kim et al. [168] reported the growth of TiO$_2$ nanowires by electrospinning. At first, TiO$_2$/poly(vinyl acetate) composite nanofiber mats were directly electrospun onto interdigitated Pt electrode arrays, hot pressed at 120 °C, and calcined at 450 °C. This resulted in a novel multiple nanowire network composed of sheaths of 200-500 nm diameter cores filled with readily gas accessible 10 nm thick single-crystal anatase fibrils. Electrospinning process for the growth of TiO$_2$ nanowires is represented in Figure 1.17.

1.2 Applications of 1-D nanostructured oxides

Metal oxide nanostructures as functional nanomaterials and nanodevices have novel properties due to size [1-6] and surface effects [7-12] and have potential applications in various fields. Some applications include gas sensors [7, 11, 12, 42, 46, 68, 81, 169], biological sensors [43, 170-172], nanoelectrodes [173-175], solar cell materials [76, 176-178], photocatalysts [167, 179, 180], nanowire-based field effect transistors and memory devices [181, 182]. In this section, some application fields will be discussed with a focus on the advantages of nanostructures.

1.2.1 Sensing applications in chemical and biological detection

Metal oxide semiconductors have been used as gas sensors for some time [183]. The fundamental sensing mechanism of metal oxide based gas sensors depends on a change in the electrical conductivity when they are exposed to a gaseous atmosphere. The
conductivity change originates from the interaction between the surface complexes such as O\(^{-}\), O\(_2\)^{-}, H\(^{+}\) and OH\(^{-}\) reactive chemical species and gas molecules in the target gas and it is this change in the conductivity which the sensor detects. The most recent research trend has been devoted toward nanostructured oxides because complete depletion of carriers in the grains can strongly modify the movement of charge carriers and enhance the sensitivity. In addition, using 1-D nanostructured oxides such as nanobelts and nanowires can give some advantages over conventionally fabricated thick film sensors. A 1-D nanostructured oxide is usually single crystal, meaning that the exposed faces will be always the same. Thus, it can guarantee the uniformity of the sensing behavior from unit to unit. Moreover, it shows higher sensitivity due to the fact that the surface to volume ratio is very high and its size is comparable to the depletion length [184].

**Figure 1.18A** shows the isothermal response of the current flowing through SnO\(_2\) nanobelts as a gas sensor [7]. Two square concentration pulses of CO (250 an 500 ppm, respectively) are introduced into the test chamber at an operation temperature of 400 \(^\circ\)C with 30 % RH (relative humidity). The electric current increases from about 60 % to 100 % with the introduction of 200 and 500 ppm CO. The sensor response, defined as the relative variation in conductance due to the introduction of gas, is about 0.9. The nanobelt sensors were capable of detecting a few ppb levels of NO\(_2\) which was difficult to monitor with conventional sensors. The ultrahigh surface area to volume ratios of these structures makes their electrical properties extremely sensitive to surface-adsorbed species. Vargese et al. [185] also reported TiO\(_2\) nanotubes for high sensitivity sensors and the sensitivity defined as \(\Delta R/R\) was reported to be on the order of \(10^3\).
Cui et al. reported a single Si nanowire FET device showing highly sensitive
detection of biological species such as streptavidin and protein [42]. It has been known
that chemical or biological species can be monitored by planar FET devices when the
species causes accumulation or depletion of charge carriers within the FET structure.
They used biotin-streptavidin to functionalize the Si nanowire and measured the
conductance change of the biotin modified Si nanowires. When they added 250 nM
streptavidin solution, the rapid increase in the conductance of the Si nanowire was
measured. These changes in conductance of the Si nanowire is given in Figure 1.19.
They argued that the increase of the conductance was caused by enhanced surface-
volume ratio and it can be beneficial using this device compared to planar FET devices
because it can be easily incorporated into human body.

1.2.2 Photocatalysis

Photocatalysis is defined as the promotion of a photoreaction under a catalyst.
Electron-hole pairs generated by photon energy is the key factor to determine the activity
of the reaction. Because the generated electron-hole pairs can easily recombine, charge
separation becomes very important. The principle of the photocatalysis is schematically
represented in Figure 1.20 [186]. The generated electron-hole pairs are used to generate
free radicals which can further continue secondary reactions. In other words, the reactive
electron reduces O₂ molecules to OH radicals, whereas the reactive hole oxidizes the
pollutant D to its radical cation. Thus, both the reductive and oxidative interfacial
electron transfer processes can induce strong oxidation of organic and inorganic
pollutants. The photocatalytic behavior was not realized until the discovery of water
electrolysis by TiO$_2$ reported by Honda [62]. Most of the photocatalysis work have been devoted to the splitting of water molecules and self-cleaning of contaminations and waste [187].

It has been known that nanostructured TiO$_2$, with high surface area and crystallinity, can enhance catalytic abilities because high surface area increases the adsorption of reactants more efficiently and crystallinity decreases the electron-hole recombination sites [63, 188]. Therefore, many efforts have been directed to create high surface, crystalline nano-structured TiO$_2$. Particles around 10 nm have been a major source for photocatalysis and the sol-gel method is generally used for synthesizing TiO$_2$ nanoparticles. TiO$_2$ nanotubes have also been studied for dehydrogenation of ethanol as well as the decomposition of gaseous isopropanol into acetone and carbon dioxide [189, 190].

### 1.2.3 Solar cell materials

A solar cell device can be defined as a device which transforms solar energy into electricity. There have been many solar cell devices which have used MEMS fabrication technology by using Si and GaAs. These devices require high cost for the fabrication, which hinder the usage and large scale deployment of the devices [191]. The use of TiO$_2$ in a solar cell devices has been an attractive research field since the report of the Graztcel cell [192, 193]. This device is also called a dye-sensitized solar cell because it consists of a dye, TiO$_2$, electrodes, and an electrolyte. A schematic view of the operating principle of the DSSC (Dye Sensitized Solar Cell) is shown in Figure 1.21 [161]. A dye (a ruthenium metalorganic dye (Ru-centered)) generates electron-hole pairs when light falls on the dye.
energy is absorbed. The generated electrons are moved to the TiO₂ and the holes are transferred to the electrolyte. The dye is subsequently recovered by electron donation from the electrolyte, usually an iodide/triiodide redox couple system. The counter electrode then resupplies the electrolyte with electrons.

TiO₂, with a high band gap energy (3.2 ev), conventionally fabricated in DSSC has the form of a nanoporous structure to ensure higher contact between the dye and TiO₂. Light absorption at the dye on nanoporous TiO₂ is higher than that on a flat TiO₂ surface. The nanoporous TiO₂ can easily change from an insulating to a conductive state without any doping.

To increase the efficiency of the solar cell, nanostructures with a high degree of order have been explored [194]. Mesoporous channels or nanorods aligned parallel to each other and normal to a glass substrate is the most desirable structure, which can promote charge diffusion in the pores or the wires. Alivisatos et al. [195] reported that hybrid solar cells made of CdSe nanorods showed a superior performance, which indicates the advantage of one-dimensional nanostructures.

### 1.2.4 Other applications

Biosensors, which utilize immobilized enzyme for the conversion of the target analytes in a biological system into electrochemically detectable products, are one of the most widely used detection methods for the determination of blood glucose [43]. Nanoporous TiO₂ films have been considered to enhance the active surface area available for immobilizing protein.
TiO$_2$ coating has been widely applied to the surface of Ti and Ti alloys which have been used as bone and dental implants [196]. Ti and Ti alloys are bio-compatible, which means that once they are inserted into human body there is no poisoning effect. However, they are not bioactive which is to say that they do not promote fast cell adhesion and growth. In order to establish the bioactivity on the surface of these metals, various surface modification methods like sand blasting, plasma spray coating, and anodization have been performed. TiO$_2$ nanostructure can increase this bioactivity. Webster et al. reported that the bioactivity was increased when nanostructured oxides such as alumina and titania, which have grains smaller than 100 nm, were used to cover the metal surface [197, 198].
Figure 1.1 A: A schematic diagram of TiO$_2$ nanowire array growth by the top down-method, B: the image of SiO$_2$ mesa and C: the image of TiO$_2$ nanowire [78].
Figure 1.1: Continued
Figure 1.2 Flow of processes to make multiple Si nanowire transistors [23].
Figure 1.3 A: An image showing a bundle of nanowires with caps on their tips, B: inner core of Si covered by amorphous SiO$_2$ sheath and C: the lattice image of a nanowire indicating that the growth direction is [111] [115].
Figure 1.3: Continued
Figure 1.4 A: SEM image of the as-synthesized ZnO nanostructures, showing strings of “tadpole like” nanostructures, B: low magnification TEM image of the as-synthesized ZnO nanowire-nanoribbon junction arrays, C: TEM image of two junctions and D: the corresponding electron diffraction pattern [70].

Continued
Figure 1.4: Continued
Figure 1.5 A: TEM image of a ZnO nanowire with an alloy droplet on its tip and B: high resolution TEM image of an individual ZnO nanowire showing its <0001> growth direction [126].
Figure 1.6 Low magnification shows some nanowires with/out Au particles; the black area corresponds to inset (a) and (b). (a) HRTEM image showing the growth direction ([110]) and (b) the SAED pattern showing rutile single crystal [127].
Figure 1.7 A: TEM image of TiO$_2$ nanowire on sapphire, showing the existence of twin along [020] and rutile phase and B: TEM image of TiO$_2$ nanowire on quartz, showing the growth direction [110] and rutile phase [79].
Figure 1.8 TEM image of SiOx nanowires grown by the SLS method [100].
Figure 1.9 Schematic depiction of the SiNW growth via the SLS mechanism: (a) deposition of a thin layer of Ni on the Si (111) substrate; (b) formation of the Si-Ni eutectic liquid droplets; (c) the continuous diffusion of Si atoms through the substrate-liquid (S-L) interface; (d) final state of the SiNW growth. The smooth surface of the original substrate becomes rough at the end of the SiNW growth [101].
Figure 1.10 A: SEM image of the as-synthesized SnO$_2$ nanobelts and B to D: TEM images of SnO$_2$ nanobelts with straight and twisted shapes and E: HRTEM image of a SnO$_2$ nanobelt showing that the nanobelt is single crystalline and free from dislocation and defects. In the inset, the corresponding electron diffraction pattern showing the growth direction to be [101] an F and G showing lattice images showing the growth directions [130].
Figure 1.11 A: SEM image shows that the sample of TiO$_2$ nanowires grew on alumina substrate with large area and B: HRTEM shows an individual TiO$_2$ nanowire and the wire was growing along [1 1 0] direction and the SAED of (1 1 0) plane shows that the nanowire was perfect single crystal and the rutile structure was verified from the SAED pattern [134].
Figure 1.12 A schematic diagram of solution-liquid-solid (SLS) growth mechanism for InN synthesis from precursors [108].
Figure 1.13 A: SEM micrographs of the bottom view of anodic alumina layers with various pore sizes A: ~ 30 nm and B: ~ 250 nm [199].
Figure 1.14 SEM images of TiO2 nanostructures obtained by immersing the template membrane in the sol for A: 5, B: 25, and C: 60 s [136].

Continued
Figure 1.14: Continued
Figure 1.15 A schematic diagram demonstrating the progress of the electrochemically induced sol gel process [156].
Figure 1.16 SEM images of a TiO₂ nanotube array sample grown from a 2.0 % HF – DMSO electrolyte for 70 hr at A, C, D: 40 and B, D, F: 60 V; Top surface images are seen in A and B, cross-section images in C and D, and tube bottom view images in E and F [161].
**Figure 1.17** Schematic diagram of the processing steps used to fabricate TiO$_2$ nanofiber mats on Al$_2$O$_3$ substrates with interdigitated Pt electrode arrays [168].
Figure 1.18 Response of the SnO$_2$ nanobelts to A: CO at a working temperature of 400 °C and 30 % RH and B: NO$_2$ at a working temperature of 200 °C and 30 % RH [7].
Figure 1.19 Real-time detection of protein binding. A: Schematic illustrating a biotin-modified SiNW (left) and subsequent binding of streptavidin to the SiNW surface (right). Plot of conductance versus time B: for a biotin-modified SiNW: region 1 corresponds to buffer solution, region 2 corresponds to the addition of 250 nM streptavidin, and region 3 corresponds to pure buffer solution, C: for an unmodified SiNW; regions 1 and 2 are the same as in B, and D: for a biotin-modified SiNW: region 1 corresponds to buffer solution, region 2 to the addition of a 250 nM streptavidin, E: for a biotin-modified SiNW, where region 1 corresponds to buffer solution, region 2 corresponds to the addition of 25 pM streptavidin, and region 3 corresponds to pure buffer solution. Arrows mark the points when solutions were changed [42].
Figure 1.20 Mechanistic principles for the degradation of pollutants [186].
Figure 1.21 Principle of dye-sensitized solar cells [186].
Table 1.1 Synthesis conditions and morphology characteristics of oxide nanostructures [128].

<table>
<thead>
<tr>
<th>Nano-structure</th>
<th>Source materials</th>
<th>Evaporation temperature °C</th>
<th>Pressure (Torr)</th>
<th>Substrate temperature °C</th>
<th>Lengths (μm)</th>
<th>Width or diameter (nm)</th>
<th>Width-to-thickness ratio</th>
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<td>~700</td>
<td>&gt;200</td>
<td>100–500</td>
<td>3–20</td>
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CHAPTER 2

LITERATURE REVIEW: MECHANISMS FOR THE GROWTH OF 1-D NANOSTRUCTURES

2.1 Introduction

The growth of nanowires by simple heat treatments under an Ar gas atmosphere containing a low oxygen concentration on various Ti alloy samples has been observed. When pure Ti or Ti alloy samples are exposed to the flowing Ar gas at 600 ~ 700 °C, these processes result in the growth of nanowires on the top of an oxide layer. The length of nanowires was in the range of a few hundreds nm to several μm depending on Ti alloy samples used. However, the diameter of nanowires seemed to be constant regardless of Ti alloy samples and ranged from 10 to 60 nm.

The purpose of current research is to establish fundamental understanding of the growth of nanowires and control the morphology of the nanowires. Many feasible mechanisms have been reported to explain the growth of 1-D nanostructures by various growth methods [98, 200, 201]. In this chapter, established mechanisms regarding the growth of 1-D nanostructures from techniques using vapor phases are presented. Even though the process developed by us has a common feature in that a gas phase, Ar gas, is
used, there would be difference between established and our method because it is found
that the growth of nanowires by our method is caused by the oxidation of both pure Ti
and Ti alloys. Therefore, the fundamental understanding of the oxidation process of pure
Ti and Ti alloys to form oxide layer or scales is given briefly. After that, the mechanisms
developed for 1-D growth are discussed. Even though the growth of nanowires by
oxidation of metal has been reported intermittently [109, 110, 112-114, 202-216], there is
no comprehensive understanding of the growth of 1-D nanostructures while some of
plausible explanation have been reported. Some of reported mechanisms for the growth
of nanowires from oxidation of metals are presented.

2.2  Crystal structures of Ti and Ti alloys

The dominant crystal structures of Ti are $\alpha$ phase (JCPDS #: 44-1294, a: 2.9505 Å
and c: 4.6826 Å ; hexagona closed pack, hcp) and $\beta$ phase (JCPDS #: 44-1288, a: 3.3065
Å ; body centered cubic, bcc). Ti shows an allotropic phase transformation at 882 °C
from $\alpha$ to $\beta$ phase at 1 atm [217, 218]. Table 2.1 summarizes basic properties of Ti
compared to Fe, Ni and Al [218]. It has a high melting temperature of 1670 °C. Even
though Ti has the highest strength at a relatively low density, the limited use of Ti is
attributed to its high reactivity with oxygen at high temperature. Applications of Ti
includes high temperature gas turbines [219], hydrogen storage [220] and dental implant
[221].

The phase of Ti can be modified by adding alloying elements such as Al, V, Mo
and Cr. It can be divided into two categories depending on the effect on the transition
temperature from $\alpha$ to $\beta$ phase. As the concentration of Al, $\alpha$ stabilizer, increases, the
transition temperature of $\alpha$ to $\beta$ phase increases as shown in Figure 2.1A [222]. $\alpha$ stabilizer is then defined as an alloying element which increases the transition temperature. $\beta$ stabilizers such as V, Mo and Cr promote formation of $\beta$ the phase as indicated in Figure 2.1B. $\alpha$ and $\beta$ stabilizers can be added together to pure Ti for the formation two-phase mixtures. The relative amount of each stabilizer determines the amount of each phase in the mixture. For example, Ti64 is a common alloy of the mixture of $\alpha$ and $\beta$ phase with 6 wt. % of Al and 4 wt. % of V.

### 2.3 Thermal Oxidation of Ti and Ti Alloys

When Ti is exposed to a gas environment containing oxygen, titanium oxides such as TiO, Ti$_2$O$_3$, Ti$_3$O$_5$, and TiO$_2$ can be formed during the oxidation. The Ti-TiO$_2$ phase diagram is represented in Figure 2.2 [223]. It is believed that the oxidation mechanism is quite complicated based on experimental results on the kinetics of oxidation and on the structure of the scaling layer. Hickman et al. [224] reported that the scaling layer was TiO$_2$ up to 800 °C. TiO was formed in the vicinity of the metal phase in addition to TiO$_2$ and Ti$_2$O$_3$ that formed in the middle region of the scaling layer above 800 °C for long oxidation times. According to Morton et al. [225], the structure of the scaling layer was divided into three temperature regions based on the results and analyses of microscopic and X-ray investigations as shown in Figure 2.3. Their results are summarized as follows.

1. For short oxidation times, the formation of TiO$_2$ with a blue color was only observed up to 800 °C.
2. There was a TiO layer formed between the blue TiO₂ layer and the metal. The initially good adherence of the oxide layer is taken away due to the considerable mutual solubility of the TiO and Ti phases.

3. A Ti₂O₃ layer was formed between 875 and 1050 °C, which was relatively thin after long oxidation times.

Because of the complicated structure of the scaling layer and the lack of quantitative diffusion data for titanium and oxygen ions in the individual oxide layer, it is difficult to understand the oxidation mechanism. Kofstad et al. [226] investigated the oxidation mechanism of titanium between 800 and 1200 °C by various techniques and the significant results are summarized below.

1. The initial oxidation is a result of the rate determining diffusion of oxygen in titanium. The activation energy from the initial parabolic rate law is 51 kcal/mole.

2. From diffusion marker studies between 800 and 900 °C, platinum markers always existed on the surface of the oxide scale. At higher temperatures, where a two layered TiO₂ scale was seen, the platinum markers were found at or close to the interface between the two TiO₂ layers. The reason for the burial of the maker may be related with recrystallization and plastic flow in the outer layer of the scale. Apart from this uncertainty in the marker experiments, it may be concluded that oxygen diffusion is the mechanism responsible for oxidation.

Even though the oxidation mechanism for titanium was achieved by the inward diffusion of oxygen, growth took place within the lamellar rutile scale by the outward
migration of titanium in an inner layer and the inward diffusion of oxygen in the outer layer of the scale according to Kofstad et al. In addition, Czerwinski et al. [227] reported that the outward diffusion of titanium cations contributed to overall transport for thin and compact single-layer oxide.

2.4 Current understanding of the growth of nanowires

2.4.1 The mechanism of the growth of nanowires by VLS (Vapor-Liquid-Solid)

When Wagner et al. [98, 228] reported the growth of single crystal Si-whisker by the involvement of an impurity by using the disproportionation of SiI₂, or by hydrogen reduction of SiCl₄ as vapor phase for the source of the growth of whisker, he referred this growth as the VLS growth because of the existence of a liquid phase. Figure 2.4 shows the schematic diagram which he proposed to explain the growth of the whisker. At first, the liquid droplet was formed resulting from the reaction between Au and Si. The purpose of introduction of Au impurity was to form a liquid alloy droplet at relatively low temperature, 363 °C as confirmed in the phase diagram by Okamoto et al. [229]. After the formation of the liquid droplet, it acted as a favorable site to direct preferential addition of the reactant (Si) from the vapor phase, which promotes the liquid to be supersaturated with Si. The whisker growth proceeds by precipitation of Si from the liquid droplet. As the growth of whisker continues, the liquid droplet rides on the tip of the whisker. He emphasized three important factors to consider: i) an impurity is required for the growth of whisker, ii) there is no axial screw dislocation in Si whiskers and iii) a small cap or globule existed at the tip of the whisker during the growth. Conventionally,
the growth of whiskers was explained by the theory proposed by Frank using screw dislocation [200]. This defect assisted whisker growth mechanism is discussed later. One of the difference between the VLS and VS mechanism is that the VLS mechanism does not require the existence of screw dislocation or axial dislocations to promote one dimensional growth because the liquid droplets provide and confine the growth of whiskers in one direction. Once the growth of single crystal Si whiskers was reported [98, 228], there have been a lot of reports following his idea about the growth of whiskers from other materials and even at nanoscale [96, 97, 125].

It is observed that the diameter of nanowires or whiskers from the VLS growth is usually comparable to that of the liquid droplet. There have been controversial about a critical radius of the liquid droplet, which can dictates the growth of whiskers or nanowires. Givargizov [230] proposed and argued that there would be no growth of whiskers even if there were liquid droplets but the radius of the droplet was bigger than a critical radius. He explained that there was a critical radius for the growth of whiskers based on the Gibbs-Thomson effect and the estimated value was around 100 nm, which implied that the critical radius of liquid droplets should be over than 100 nm for the continuation of the growth of 1-D nanostructures. However, this critical radius limit was not valid when Si nanowires with the diameter of less than 20 nm were reported by Lieber et al [30, 231].

There have been efforts to determine the critical radius of the liquid droplet and the critical radius of the liquid droplet based on the experiments using a laser to generate a mixed vapor of Si and Fe is determined by [128]
\[ r_{\text{min}} = \frac{2\alpha V_L}{RT \ln \sigma} \]  
\hspace{3cm} (2.1)

where \( \alpha \) is the liquid-vapor interface energy, \( V_L \) is the molar volume of the droplet and \( \sigma \) is the degree of supersaturation of the mixed vapor. Based on the equation (2.1), the critical radius increases as the interface energy increases and the supersaturation degree decreases.

According to the classic theory of nucleation and growth for a general solution synthesis route, the free energy of the formation of a nucleus on a substrate is given by [232]

\[ \Delta G = -RT \ln S + \sigma_{cl} + (\sigma_{cs} - \sigma_{sl}) \sigma_{cs} \]  
\hspace{3cm} (2.2)

where, \( S \) is the degree of supersaturation, \( \sigma_{cl} \) is the interfacial energy between the nucleus and the liquid, \( \sigma_{cs} \) is the interfacial energy between the nucleus and the substrate, \( \sigma_{sl} \) is the interfacial energy between the substrate and the liquid, and \( A_{cs} \) is the surface area of the particle. For the VLS growth, the equation (2.2) needs to be modified and the equation for the VLS is presented by

\[ \Delta G = -RT \ln S + \sigma_{cv} + (\sigma_{cs} - \sigma_{sv}) \sigma_{cs} \]  
\hspace{3cm} (2.3)

where, \( \sigma_{cv} \) is the interfacial energy between the nucleus and the vapor, and \( \sigma_{sv} \) is the interfacial energy between the substrate and the vapor. Figure 2.5 is a schematic plot of the number of nuclei (N) as a function of degree of supersaturation, S. It is realized that there is a narrow region for the growth of 1-D nanostructures. The growth of nanostructures is hindered at a high degree of supersaturation because of a high degree of precipitation while there is no growth of nanostructures at a low degree of
supersaturation. By taking into consideration of these, a few design rules for the growth of nanostructures can be deduced as follows.

1. Massive precipitation is not likely to produce the growth of nanostructures. Therefore, it is required to decrease the temperature and concentration of the reactant for the growth of nanostructures.

2. It is required to reduce the interfacial energy between the substrate and the nucleus. This approach is more practically performed by generating large number of nuclei on the substrate. Consequently, there is a minimization of the energy barrier for the subsequent growth of nanostructures.

3. There should be the preference of oriented kinetic growth of nanostructures to non-oriented nanostructures.

The reaction temperature and concentration of the reactant can be determined by taking into consideration of the binary phase diagram between the reactant and the catalyst. For the growth of Si nanowires, if the catalyst of Fe is used as the agent to form liquid droplets, the reaction temperature should be approximately at 1207 °C as shown in Figure 2.6 assuming that the melting temperature is not affected by the size of the nucleus. However, there have been reports about the decrease of the melting temperature when the size of the particle reaches nanometers[233]. For instance, the melting temperature of Au nanoparticles was reported to be less than 200 °C when the size of them was around 5 nm. Therefore, it should be considered that the reaction temperature can be decreased by the effect of the particle size.
The existence of a metal cap at the tip has been used to identify the growth of nanowires by the VLS method. Even though Law et al. [234] addressed that the caps can be removed because of interfacial dewetting and large interfacial thermal expansion differences during cooling, there are few reports about the dislodge of the caps during cooling. According to Lee et al. [79], the growth of titania nanowires on either a sapphire or silica substrate was obtained by using Au catalyst. However, there was no cap on a nanowire in the TEM image as shown in Figure 1.7. It is also worth noting that there is no eutectic phase between Ti and Au at a substrate temperature of 1050 °C, as shown in Figure 2.7. Au catalyst existed as a liquid phase at the temperature, but its role as a catalyst is yet be understood. Because there was no detail mention about the disappearance of Au catalyst and chemical analysis of the nanowire, it is hard to determine how the disappearance occurs.

Even though it is commonly believed that the existence of liquid phase for the growth of nanowires is necessary as discussed previously, recently there were a few reports about the possibility of the growth of nanowires by solid phase of catalysts rather than liquid phase: TiSi₂ catalyzed Si nanowires [235], SiOₓ catalyzed InAs [236] and Al catalyzed Si [237]. The growth by these solid phase catalysts is called Vapor-Solid-Solid (VSS) because there are no liquid phase catalysts as observed in the VLS. For example for Al catalyzed Si, Figure 2.8A shows a schematic of the Al-rich region of the Al-Si binary phase diagram for either the VLS or the VSS. The growth of nanowires by the VSS occurred below 577 °C. To produce Si nanowires by the VSS, the diffusion of Si through a layer/particle of solid Al should occur at the temperature for the VSS growth. The
possibility of the growth of nanowires was verified by using the relation between the concentration gradient and the diffusion of Si through the solid Al catalyst particle to the Si nanowires [237],

$$\Delta C = \frac{Dv}{r \rho \nu \Delta}$$

(2.4)

where, $\rho$ is the atomic density, and $\nu$ is the growth rate of a nanowire, $r$ is the radius of the particle and $D$ is the diffusion constant for Si in solid Al. The temperature for the growth of Si nanowires by the VSS was $430 \, ^\circ\text{C}$ and the values for $\rho$, $\nu$, $r$ and $D$ are $5.0 \times 10^{-23} \, \text{cm}^{-3}$, $0.3 \, \text{nm} \, \text{s}^{-1}$, $17 \, \text{nm}$, and $1.54 \times 10^{-14} \, \text{m}^2\text{s}^{-1}$, respectively. The estimated concentration gradient matched with the value reported [238], which indicated that the growth of Si nanowires was achieved by the diffusion of Si in the solid Al particle. One other interesting observation to notice was the occurrence of tapering of the nanowires, which was explained by the temperature gradient along the nanowires as seen in Figure 2.8B.

**2.4.2 The mechanism of the growth of nanowires by VS (Vapor-Solid)**

There have been a lot of reports about the growth of nanowires, nanorings, and nanobelts by the VS even though the growth mechanism is in dispute. As previously mentioned, there were attempts to establish the growth of nanowires by the VS with the theory proposed by Frank et al. [200]. As a screw dislocation terminates the growth surface of the whisker, the spiral step around the dislocation supplies preferred sites for continuous stacking of atoms at a low energy. Sears et al. [201] further extended the theory to explain the growth of whiskers. Figure 2.9 shows a schematic diagram of a whisker growth on a screw dislocation. They propose that there are 3 stages for the
growth of whiskers by a screw dislocation. At the first stage as shown in Figure 2.9A, screw dislocations emerge at the surface and a screw dislocation, which is separated from its neighbor, form a growth cone and produces a smoothly advancing surface because screw dislocations act as a deposition sink. The distance between steps at the cone becomes smaller as shown in Figure 2.9B because of the faster diffusion to the tip of the cone. After that, a columnar or pillar is shown at the base of the cone as shown in Figure 2.9C. This screw dislocation aided growth of ZnO nanowires reported by Wang et al. [239] is shown in Figure 2.10. They explained that when a dislocation propagate in a perfect crystal, the dislocation cannot terminate inside the perfect crystal. It can end on either a defect inside the crystal or on a surface. If a screw dislocation terminate on a surface, a step forms at the emerging point of the dislocation. As led by the dislocation, growing nanowires can wind into a spiral feature as shown in Figure 2.10B. The growth of ZnO nanowires is largely enhanced because there is no requirement of nucleation of fresh surface steps. Even though there are many reasons for the generation of a dislocation, oxygen atoms may cause the nucleation of a dislocation for Si nanowires [240]. It is believed that screw dislocations have been responsible for the formation of the dendrite or whisker. Winding feature at whisker tips caused by screw dislocation indicates that dislocations exist when the diameter of nanowires is bigger than 200 nm as shown in Figure 2.10B. However, for nanowires having the diameters less than 200 nm, it is realized that there is no evidence of screw dislocation, indicating that nanostructures are dislocation free. These lack of evidence of the existence of screw dislocation for
nanowires or whiskers having a diameter smaller than 200 nm causes to look for an alternative mechanism.

ZnO nanobelts grown by the VS was explained by the mechanism proposed by Wang et al. [128]. A schematic diagram of the mechanism is presented in Figure 2.11. For the vaporization of ZnO, ZnO powder was heated over 1000 °C and the source material is vaporized into molecular species which consist of the stoichiometric cation-anion molecules such as ZnO. The vaporized species travel in a reactor and condense on a substrate at a lower temperature, which indicates that the driving force for the growth of 1-D nanostructures is a temperature gradient. During the condensation, the molecular species are deposited in a way that the local charge and structural symmetry is preserved as shown in Figure 2.11D and then form a small nucleus, while the surfaces which have lower energies begin to form, such as the side surfaces. Because high temperature causes the mobility of the molecules/atoms to be high and then the low energy surface tends to be flat, newly coming molecules onto the surfaces do not stick to the side surfaces but accumulate on the rough growth front as seen in Figure 2.11E-F. The rough structure of the tip or growth front promotes a fast accumulation of incoming molecules, resulting in the growth of nanobelts after some time. The mechanism was supported by the evidence of the TEM images of the tips of nanobelts as shown in Figure 2.11A-B. The growth front is a round shape, indicating that there is atomic scale roughness caused by the presence of steps, ledges and kinks. Therefore, the newly arriving molecules are stuck on the growth front and continue the growth of nanobelts. It is worth noting that even though the newly arriving molecules can be accumulated on both the rough growth front and the
side surfaces, molecules stuck on the side surfaces move to the growth front because the molecules randomly diffuse on the surfaces and finally stay at the lower energy sites at the growth front. Wang et al. argued that the growth of nanobelts is dominated by kinetics rather than thermodynamics.

The other plausible mechanisms for the growth of 1-D nanostructures by the VS mechanism are inherent anisotropic growth and defect induced growth such as by a twin. The growth of nanowires, nanobelts and nanorods is resulted from the preferential reactivity or binding of gas reactants on the specific surfaces according to the argument by Wang et al. [239]. However, the difference of the preferential reactivity on each surface is not significant, which indicates that the degree of anisotropic properties of crystals is not large enough to cause the aspect ratio of 1000 usually observed in the growth of nanowires. For TiO₂, reported difference of the reactivity on each surface is not large [241]. For pure Ti, the activation energy of oxygen adsorption on (0001) surface of α-Ti single crystal is reported to be 760 cal/mol [242]. Although there are no reports about the energy on other surfaces, the energy would not be hugely different to allow the growth of nanowires. Even though the growth of 1 D nanostructures by anisotropic difference is difficult to observe among many oxides, Wang et al. [239] reported the growth of ZnO nanowire as shown in Figure 2.12A and C. The grown nanowires show hexagonal tips which maintain their base hexagonal structure (Wurzite structure) but the length of the nanowires is over 5 μm. Consequently, Wang argued that there would be anisotropic growth rate differences between the longitudinal and perpendicular directions, thus resulting in 1 D nanowires based on this observation.
The other possibility for the growth of 1-D nanostructures is related with defects such as a twin. Even though the roles of defects such as twins and stacking faults are not known, several aspects can be considered for the growth of 1-D structures. As discussed in the mechanism proposed by Frank and Sears, the role of defects is to provide favorable site for the growth and fast nucleation [200, 201]. The growth of a crystal continues by the addition of atoms to the kink sites of a surface step. As the kink advances along the surface by the addition of atoms, the growth of 1-D nanostructures proceeds perpendicular to the surface. The growth of ZnO nanowires by twin is represented in Figure 2.12C and E.

There was a report about the growth mechanism of nanorods without a catalyst by Kown [243]. He argued that after the critical radius limit of nuclei is satisfied, the growth of nanorods can proceed in two ways: isotropic expansion or anisotropic growth. The growth mode can be determined by whether the momentary volume of incident adatoms supplied from a gas phase, $\delta v$, is greater than a certain threshold volume [243]. The threshold volume can be calculated by obtaining the ratio of the surface energy gains of the rod-shape nucleus, $\delta F_1$, to the surface energy gains for isotropic expansion, $\delta F_2$, within the momentary volume of $\delta v$. The quantities $\delta F_1$ and $\delta F_2$ are expressed by

$$\delta F_1 = 2\pi \gamma R^2 (1 - \cos \theta) + 2\gamma \delta v / R \sin \theta$$

$$\delta F_2 = 2\pi \gamma (1 - \cos \theta) [3\delta v / \pi (1 - \cos \theta)^2 (2 + \cos \theta) + R^3]^{2/3}$$

where, $\gamma$ is the surface tension of the adatom and $\theta$ is the contact angle of the adatom on the substrate. Figure 2.13 shows the theoretical behavior of $\delta F_1/\delta F_2$ as a function of $\delta v/R^3$ for the value of $\theta$ of 60°. When the value of $\delta V/R^3$ is smaller than the critical
value, $\delta v_c/R^3$ ($\delta F_1 / \delta F_2 = 1$ when $\delta v_c/R^3 = 2.65$ with $\theta = \pi/3$), the nucleus prefers anisotropic growth, while it follows an isotropic manner for the further growth when $\delta v/R^3$ is larger than $\delta v_c/R^3$. $\delta v_c/R^3$ can be calculated by equating $\delta F_1$ and $\delta F_2$. $\delta v_c/R^3$ is smaller than 3.03 when it is plotted as a function of $\theta$ as in the inset of Figure 2.13. Therefore, a reaction with a relatively slow supply (smaller reactant dose satisfying the condition of $\delta v_c/R^3 < 3.03$) of the reaction precursors is more likely to lead to an anisotropic morphological transition than that with a fast supply. Consequently, this anisotropic growth mechanism produces the wire or rod-shaped structures. This effect of the flow rate on the morphology was observed in the case of Si-C-N nanorods [244] as shown in Figure 2.14. As the flow rate increased over 50 sccm, the growth mode followed the isotropic manner and the surface morphology was micro/nanocrystals without 1-D nanostructures.

2.4.2 The mechanism of the growth of nanowires by metal oxidation

According to Pfefferkorn [245], a crystal needle forest was formed on the surface of phosphorus bronze oxidized at 430 °C for 1 hour. He believed that the appearance of these crystal needles and lamellae was due to a preferred growth direction and surface diffusion. Paidassi [246] also reported that the formation of iron oxide needles was observed during the oxidation of iron. Even though the process was not oxidation, Fischmeister et al. [247] reported experimental results on the formation of needles of Ag$_2$S during sulfidation of silver. They argued that the formation of these needles could be due to the limited supply or transport of the gas. Recently, cupric oxide (CuO) nanowires or whisker growths have been reported [112, 203, 206, 208, 214, 215] and
their growth behaviors seem to be very similar to this work. The growth of these cupric oxide nanowires is related with the oxidation of Cu because the vapor pressure of Cu at 500 °C is not high enough to fabricate these nanowires. However, some researchers reported that the growth of CuO nanowires is related with the initial formation of Cu₂O. Cu₂O phase can sublime at 600 °C with the vapor pressure of 10⁻⁴ torr which is enough to produce nanowires [248]. However, it was argued that the growth of CuO nanowires was not related with Cu₂O phase according to Kaur et al. [208]. They checked the cold end of their tube and tube wall to identify deposition of Cu₂O and they found nothing. In addition, they made Cu₂O templates and oxidized directly to check if there would be the growth of CuO nanowires and then they found no nanowires. Another interesting observation from literature is that the growth of CuO nanowire is closely related with the location on a sample. Xu et al. performed CuO nanowire growth in wet air by oxidization [249]. What they found was that the alignment and density of nanowires on different location was affected by the velocity vectors of local gas flow. They announced that the growth of nanowires was controlled by the local gas flux, which caused the different transport of the gas depending on the location of the sample. Their results can be translated into the understanding that the transport of oxygen or gas can affect the growth of nanowires. Kaur et al. [208] reported that there were difference between the length and diameter of CuO nanowires depending on the locations of a sample. The diameter and length of CuO nanowires on valleys located on a lower surface were in the range of 0.1 – 0.2 and 1 – 4 μm, respectively. The diameter of CuO nanowires on hills located on a higher surface ranged from 0.01 to 0.5 μm and the length of the nanowires was in the
range of 7 to 15 μm. This difference also indicates that there would be effects of the supply or transport of the gas on the growth of nanowires. Peng et al. [210, 211] reported the growth of TiO$_2$ nanowires by oxidation and they believed that the growth of TiO$_2$ nanowires was accomplished by oxidation because of the low vapor pressure of Ti. Based on these observations along with consideration that the vapor pressure of Ti is low at our processing temperature, the growth mechanism of our method can be related with thermal oxidation of titanium or titanium alloys.

Based on the reports, it is worth noting that at first an oxide layer is formed and then the growth of the metal oxide starts on top of the layer, which indicates that there is a transition from a lateral oxide formation to 1-D growth of the oxide. The reason for the transition is still not well understood and requires further investigation. For the growth of 1-D nanostructures by metal oxidation, there should be the transport of the cation to the tip or the anion to the base of a nanowire. Varghese et al. [114] reported the growth of Nb$_2$O$_5$ nanowires by the metal oxidation process. Their argument is that the growth of nanowires is achieved by the diffusion controlled tip growth mechanism. Wen et al. [111] and Srivastava et al. [209] reported the growth of α-Fe$_2$O$_3$ nanowires. Srivastava et al. found that the growth of nanowires was maximized in terms of the density and the length of nanowires at 700 °C in ozone-rich environment for 2 ~ 4 hours. They ruled out the possibility of the VLS and VS growth because the annealing temperature, 700 °C, is much lower than the melting temperatures of iron and α-Fe$_2$O$_3$ (1535 and 1350 °C) and the caps at the tips were not observed. The growth mechanism for α-Fe$_2$O$_3$ was proposed based on a stress driven mechanism. When a thin layer grows on top of a substrate that
has quite a different lattice constant, then in an attempt to minimize the total strain energy between the lattice, the thin layer spontaneously orders or self assembles into quantum dots that can take the shape of pyramids or tetrahedron or some other shape depending upon the crystal growth direction and related energetics. Large stress accumulated in the multiscale oxide growth. The porosity provided a path to release that stress in the form of other structures. These nucleating sites may also accelerate the material transport to themselves due to their very low energy, leading to a positive gradient of transporting material away from the nucleating site, which would further result in the decreasing density of the nanowires away from the nucleating sites. A similar stress driven formation of silicon nanowires has been reported by Prokes et al. [250].

Wen et al. [204] argued that there was a large influence of the rate of oxidation on the nucleation and growth of 1-D nanostructures as the flowing gas varied. What they found that in the static laboratory air, interconnected rod like structures were formed and the at a fixed flow rate (25 sccm), the different PO₂ in a gas caused different morphology. Well aligned Fe₂O₃ nanobelts were formed all over the surface under the gas mixture of O₂ (5 sccm) with N₂ (20 sccm). Wire like features were obtained under the pure O₂ condition with a low nanowire density. They also ruled out the growth of nanowires by the VLS and VS because of the same reasons as those of Srivastava [209]. One interesting point from his results is that the transition from nanobelts formed at a low temperature to nanowires formed at a high temperature. He believed that the transition of the morphology depending on the temperature is related with the surface energy and different growth rates along different crystal directions. Even though both Wen et al.
[111] and Srivastava et al. [209] reported that the growth of nanowires was related with defects or stress, the diffusion of cation or anion was still valid for the growth of nanowires. In addition, Peng et al. also proposed the growth mechanism of TiO$_2$ nanowires by oxidation process. The schematic diagram of their proposed model is given in Figure 2.16. They believed that the supply or amount of active oxygen for oxidation played a key role in producing TiO$_2$ nanowires. When formic acid was used for oxidation, there were plenty of active oxygen species for oxidation, thus resulting in thick continuous layer of oxide as shown in Figure 2.16B-1. As they used ethanol or acetone for an oxidizing gas, they argued that the active oxygen species were limited in quantity, which caused well aligned nanowire growth as seen in Figure 2.16B-3. They believed that the diffusion of Ti was established along the grain boundaries and the growth of nanowires was obtained by the outward diffusion of Ti. Consequently, the growth of nanowires by metal oxidation essentially requires the diffusion of either the cation or the anion.
Table 2.1 Some important properties of titanium and titanium alloys compared to Fe, Ni and Al [218].

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<th>Ti</th>
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<td>Low</td>
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CHAPTER 3

FORMATION OF TiO₂ NANOWIRES ON PURE Ti AND Ti ALLOYS UNDER A LIMITED SUPPLY OF OXYGEN

3.1 Introduction

Much attention has been paid to nanostructured oxides because of their interesting electronic, photonic, catalytic, chemical, and bio-chemical properties at the nano-scale. Among metal oxides, titania (TiO₂) is one of the most extensively studied transition metal oxides that have been widely used in gas sensors [12, 164], dye-sensitized solar cell [176-178], biosensors [43, 44], biocoatings [197, 198], and future memory devices [17, 18]. It is believed that using nanostructured oxides in these applications can improve their functionality and properties. The belief is based on observations that show drastically different properties of nanostructured oxides compared to their bulk counterparts [1, 7, 11]. The reason for these unique properties is attributed to quantum confinements, modified surface electronic states, different transport mechanism, and enhanced surface area. The improvement of the devices can be performed by incorporating nanostructures such as nanobelts, nanorods, nanorings, and nanotubes into the products. There have been
many attempts to fabricate nanostructured oxides, especially titania by various approaches [80, 136, 137, 156, 168]. However, the limitation in low-cost, rapid mass production, and controlling desired surface features by these approaches are the main causes for slow progress in the utilization of the devices using nanostructures. Therefore, a critical need exists to fabricate well-defined nanostructured surface features for large scale production by a simple method without any expensive equipment or expertise.

Recently, the fabrication of nanowires on pure Ti substrates was reported by annealing the samples under a limited supply of oxygen environment such as acetone [210, 211]. Peng et al. argued that the growth of nanowires was believed to be accomplished by the diffusion of Ti under a limited supply of oxygen caused by using acetone as oxygen source [210, 211]. This metal oxidation process allows highly scalable production of nanowires without any catalysts. The process also does not require any complicated and expensive equipment for the fabrication. This observation led to investigate the possibility of the growth of nanowires under an Ar gas containing a very low oxygen concentration (100s of ppm). The growth of nanowires was successfully obtained by this method on various metal substrates and is overviewed in this chapter.

3.2 Experimental

Commercial Ti (Online Metal Shop, NJ, Grade 2) and Ti64 (Online Metal Shop, NJ, Grade 5, Ti-6 wt % Al- 4 wt % V) bars with a diameter of 0.25 inch were used for the experiments. β-Ti (5-5-5) (Ti-5 wt % Al- 5 wt % V-5 wt % Mo -3.5 wt % Cr-0.5 wt % Fe) bars were also prepared by Soumya Nag and John Folz. Ti, Ti64, and β-Ti bars were
cut using a diamond blade and mechanically polished by using SiC sand papers having grit size up to 1200. The pieces were then ultrasonicated for 5 minutes in acetone and methanol, respectively and then rinsed in DI (Deionized) water. The samples were immersed in 30 wt % of HCl in DI water for 10 minutes at 80 °C to gently remove native oxide layers and then residual water and chemical solution droplets were blown away by an air gun and dried for 1 day. The samples were inserted into a quartz tube with a diameter of 1 inch for gas heat treatments and the tube was purged by an Ar (Purity: 99.998%, Praxair) gas flow with a flow rate of 1000 ml / min for 1 hour to remove residual gases. The sample was heated to a target temperature of either 600 or 700 °C with a ramping rate of 30 °C/min. The temperature of the furnace was maintained at the target temperature for a certain time duration with a particular Ar gas flow rate of 200 or 1000 ml/min. The flow rate of Ar (99.998%) was maintained by a manual gas flow meter and the oxygen partial pressure in the gas was monitored by an oxygen sensor (CG-1000, AMTEK). The humidity was also monitored by an humidity sensor (HMP234, Vaisala).

The value of the oxygen concentration for Ar gas at 1000 mL/min is approximately 400 ppm ~ 500 ppm, which is approximately equal to the partial pressure of PO₂ of 10⁻⁴ atm. Following the heat treatment, the sample was cooled down to room temperature rapidly by turning off the furnace and avoid oxidation during the cooling process while keeping the sample inside the tube and flowing the Ar gas into the tube. The schematic diagram of the experimental set up is shown in Figure 3. 1.

A field emission scanning electron microscope (FE-SEM, Model XL-30, Philips) was used to characterize the surface morphology of the metal specimens before and after
exposure to the Ar gas treatment. A high resolution SEM (FE-SEM, Sirion, FEI), was used to detect the change in the surface morphology at nanoscale. EDS (Electron dispersive spectroscopy) was also used to obtain chemical composition analyses. For SEM observations, a thin layer of gold was deposited on the heat treated samples to avoid charging effects.

The structure and chemical analyses of nanowires after heat treatments on various samples were examined with a transmission electron microscope (HRTEM, Model TF20, FEI). The nanowires were collected on a TEM grid by scraping the specimen with a glass needle. The other method to obtain TEM sample was to put the specimen in methanol and vibrate the sample by ultrasonication (FS 60 ultrasonic bath, Fisher Scientific) for 10 minutes. The dislodged nanowires were then collected on a carbon-coated copper TEM grid. These samples were used for TEM analysis via imaging, EDS, and SAED (Selected Area Electron Diffraction).

The weight change of a β-Ti substrate during a heat treatment process was measured by a thermo-gravimetric analyzer (Pyris TGA, PerkinElmer, Boston MA). A β-Ti substrate was cut to a size of 5mm×5mm×5mm (surface area: 25 mm²) and then a hole was drilled into the sample. The sample was hung by a platinum wire inserted through the hole. The heating rate was 30 °C/min to the desired temperature of 700 °C and this temperature was maintained for 6 hours. The gas flow rate was 500 ml/min and the PO₂ was 10⁻⁴ atm, as measured by the oxygen sensor.

The phase identification of the samples before and after the heat treatments were performed by an X-ray diffractometer (XRD, PAD-2000 diffractometer, Scintag). Cu Kα
(\(\lambda=1.549\ \text{Å}\)) radiation was used for the XRD analyses with 45 kV and 20 mA. The samples were scanned from 20 to 70 degrees in terms of 2\(\theta\) values with a step of 0.003 degree.

### 3.3 Results and Discussion

#### 3.3.1 Discovery of TiO\(_2\) nanowire on pure Ti substrate

Figure 3.2A shows the surface image of as-polished pure Ti (CP-Ti) samples. There was no sign of any nanostructure, but scratch marks formed during the polishing process were observed. The grain structure was not observed because there was no thermal annealing and chemical etching to reveal the grain structure in the sample. The temperature of the heat treatment was 600 °C for 8 hours under an Ar atmosphere. The flow rate for the Ar gas was 200 ml/min. The purity of the Ar gas was 99.998 % and the level of humidity remained below 0.3 % RH (Relative Humidity) during the heat treatment to minimize the effect of water vapor because water vapor has been known to promotes the formation of whiskers or needles during oxidation processes even though the role of water vapor is not yet understood [249]. Figure 3.2B shows the surface image of a CP-Ti sample after the Ar heat treatment. Nanowires formed all over the surface with a very low density. The density of the nanowires was estimated to be approximately 30 wires/\(\mu\text{m}^2\). The length of the nanowires was roughly in the range of 100 nm – 300 nm. The diameter of the nanowires ranged from 20 to 40 nm as shown in Figure 3.2C. The directions of the nanowires were randomly oriented and they were not perfectly normal to the surface of the substrate. It was observed that the growth of nanowires started from an
oxide layer which was located below the nanowires. The oxide layer consisted of very fine particles which were in the range of 10 to 20 nm. These results are very similar to those obtained at 650 °C for 1.5 hours by Peng et al. [210, 211]. They also reported that the growth of nanowires was maximized at the heat treatment temperature of 850 °C. This heat treatment temperature is very close to the transition temperature (880 °C) of CP-Ti from α to β phase Ti and this fact led us to investigate the effect of phase of Ti on the growth of nanowires.

First, it was tried to accomplish the growth of nanowires on pure β-phase Ti. A pTi sample was heated to 900 °C and then held for 1 hour which was a little shorter duration than that of the heat treatment reported by Peng et al [210, 211]. However, the shorter time would be compensated by the heat treatment temperature, 900 °C, which was 50 °C higher. The surface image after the heat treatment at 900 °C for 1 hour is presented in Figure 3.3A. The microstructure seemed to be very porous and micro-sized narrow walls were connected to each other. One interesting observation from the image shown in Figure 3.3B is the existence of steps on the surface of the wall structure. It was reported that the growth of TiO₂ was promoted by the formation of ledge or steps during oxidation [227] and these steps may be interpreted as the progression of oxidation of Ti samples. The growth of nanowires on pTi samples was not observed at 900 °C. It is concluded that the growth of nanowires from the heat treatment of pTi samples under the Ar gas atmosphere at 600 °C rather than 900 °C is only accomplished. The results of pTi samples heat treated at other temperatures are discussed in the chapter 4 but there were no nanowires formed after samples heat treated at other temperatures except 600 °C.
Consequently, it is concluded that the growth of nanowires from pTi after Ar heat treatment was only achieved at the heat treatment temperature of 600 °C. This conclusion is contradictory to that of Peng et al. who reported that the growth of nanowires was optimized at the heat treatment of 850 °C under an acetone atmosphere [210, 211]. This discrepancy may be originated from experimental condition differences because they used acetone gas as an oxygen source but the Ar gas was used as the source of oxygen in our processes. The adsorption property of acetone depending on the faces of TiO₂ rutile may be anisotropic, thus causing directional growth of nanowires under this environment.

3.3.2 Growth of nanowires on Ti64 and β-Ti (5-5-5) substrates

As mentioned earlier, it is interesting to investigate the effect of the phase on the growth of nanowires. However, the results of pTi samples at 900 °C indicates that the growth of nanowires at a heat treatment temperature which is higher than the transition temperature, 880 °C, is not favored. Therefore, it is suggested to lower heat treatment temperature, which can prevent the growth of bigger grains or particles. Unfortunately, there are no pure β-Ti at lower temperature than the transition temperature without β-stabilizers such as V, Mo, and Cr to observe solely the effects of phase of Ti on the growth of nanowires. It is hard to interpret the effects of β-phase without ignoring the effect of alloying elements such as V, Mo, Cr, and Al. Keeping in mind that there are additional effects of alloying elements, Ti64 samples were heat treated at 700 °C for 8 hr at an Ar gas flow rate of 1000 ml/min to observe if nanowires were produced after the heat treatment. The growth of nanowires was observed all over the surface as seen in
Figure 3.4A. The length of nanowires was in the range of 5 to 10 μm and the diameter was approximately in the range of 30 to 60 nm as shown in Figure 3.4B. It was realized that the diameter of nanowires from Ti64 sample was almost in the same range as that of pTi samples. It is known that Ti64 is a mixture of α and β phase and the dominant phase is α-phase [222]. Depending on the heat treatment and mechanical treatments of Ti64 samples, one achieves a variety of microstructures [252, 253]. To reveal the microstructure of Ti64 samples, Ti64 was chemically etched. The solution for etching was prepared by mixing DI water, nitric acid, and hydrofluoric acid with the volume percent of 46, 3, and 1, respectively. Ti64 was immersed in the solution for about 1 min and then rinsed in DI water. The surface image of an etched Ti64 sample is presented in Figure 3.5A. The darker part is β-phase and the lighter region is α-phase. Even though there is the effect of height difference on the contrast of the surface image, protruding region is α-phase because α-phase globules structure is usually located around the grain boundaries. An etched Ti64 sample was then heat treated at 700 °C at a flow rate of 1000 ml/min for 2 hours, which prevents longer nanowires so that the preferential growth of nanowires on each phase can be observed. From the surface image presented in Figure 3.5B, the growth of shorter nanowires was only observed in regions having the mixture of α and β-phase. At regions of the globules α-phase, there were no nanowires. As shown in Figure 3.5C, the length of nanowires was less than 300 nm and nanowires seemed to be very straight and acicular shape. Consequently, α-phase was not well suited for the growth of nanowires and the mixture of α and β-phase was better for the growth of nanowires. The reason that the growth of nanowire is better in β-phase than α-phase may
be related to the diffusion kinetics. As shown in Figure 3.6 the diffusions of oxygen and titanium are approximately $10^2$ and $10^4$ and times faster than those in $\alpha$-phase respectively.

A question arises regarding the effects of dominant or mostly $\beta$-phase on the growth of nanowires. $\beta$-phase dominant Ti (5-5-5) samples were used for heat treatments. Figure 3.7A shows the surface image of a polished $\beta$-Ti sample before a heat treatment. A rough surface was represented by the polishing process and there were scratch marks due to polishing. There were no signs of any noticeable structures before the heat treatment. After the heat treatment at 700 °C for 8 hours at flow rate of 1000 ml/min of the Ar gas, the surface morphology was drastically changed. Nanowires were formed all over the surface except at small patches believed to be $\alpha$-phase as shown in Figure 3.7B. Figure 3.7C indicates that the length of nanowires was in the range of 1 to 3 μm and the diameter of nanowires seemed to be in the same range as those of pTi and Ti64 samples. Comparing the results of $\beta$-Ti (5-5-5) and Ti64 to pTi samples, it was concluded that the growth of nanowires was better for the $\beta$-phase or the mixture of $\alpha$ and $\beta$-phases. Even though the growth of nanowires on pTi samples was still possible, the density and the length of nanowires was much improved in both Ti64 and $\beta$-Ti (5-5-5) samples.

### 3.3.3 Characterizations of nanowires grown on pure Ti

When Ti is exposed to an environment containing oxygen gas at an elevated temperature, it forms titanium oxides and the free energy of reaction for each oxide can
be calculated. There are three commonly observed titanium oxides after oxidation of pTi.

The first possible reaction to generate TiO is \[ \text{Ti (s)} + \frac{1}{2} \text{O}_2 (\text{g}) = \text{TiO (s)}, \Delta G^{\circ}_{973K} = -471.8 \text{ kJ/mol.} \] (3.1)

Two other possible reactions to produce Ti$_2$O$_3$ and TiO$_2$ are

\[ 2\text{Ti (s)} + 3/2 \text{O}_2 (\text{g}) = \text{Ti}_2\text{O}_3 (\text{s}), \Delta G^{\circ}_{973K} = -1274.0 \text{ kJ/mol,} \] (3.2)

\[ \text{Ti (s)} + \text{O}_2 (\text{g}) = \text{TiO}_2 (\text{s}), \Delta G^{\circ}_{973K} = -739.6 \text{ kJ/mol.} \] (3.3)

Assuming that there is one mole of oxygen gas, the Gibbs free energies of each chemical reaction can be compared to identify which oxide formation is thermodynamically most favored. The most favored oxide is TiO, and then followed by TiO$_2$ and Ti$_2$O$_3$. The oxygen partial pressure in the quartz tube is measured to be $10^{-4}$ atm. The theoretical oxygen partial pressures for each reaction can be calculated using the following equations

\[ \Delta G_{(3.1)} = \Delta G^{\circ}_{(3.1)} + RT \ln \frac{a_{\text{TiO}}}{a^n P_{\text{O}_2}^{3/2}} \] (3.4)

\[ \Delta G_{(3.2)} = \Delta G^{\circ}_{(3.2)} + RT \ln \frac{a_{\text{Ti}_2\text{O}_3}}{a^n P_{\text{O}_2}^{3/2}} \] (3.5)

\[ \Delta G_{(3.3)} = \Delta G^{\circ}_{(3.3)} + RT \ln \frac{a_{\text{TiO}_2}}{a^n P_{\text{O}_2}} \] (3.6)

Assuming that the activities of Ti and each oxide are unity, the calculated oxygen partial pressures of TiO, Ti$_2$O$_3$ and TiO$_2$ are $4.84 \times 10^{-102}$, $1.198 \times 10^{-31}$ and $2.318 \times 10^{-40}$ atm, respectively. Comparing these calculated oxygen partial pressures to the measured oxygen partial pressure, $10^{-4}$ atm, the direction of chemical reactions (3.1), (3.2) and (3.3) can be determined. The measured oxygen partial pressure is higher than the calculated
value for each reaction, which indicates that the chemical reactions always proceed forward. Therefore, it is believed that the formation of each oxide is possible at the oxygen partial pressure of $10^{-4}$ atm. Consequently, when nanowires were formed on pTi samples after the heat treatment at 600 °C for 8 hours, the possible phase for nanowires can be any of the titanium oxides.

The XRD analyses were performed on polished pTi samples before and after the heat treatment as shown in Figure 3.8. Before the heat treatment, the peak positions of bare polished commercially pure Ti (CP Ti) match with XRD patterns for pure $\alpha$-Ti (JCPDS #: 44-1294, hexagonal structure). It was realized that even though the peak of (101) for pTi samples is supposed to have the strongest intensity, the strongest peak occurred at (002). This discrepancy may be attributed to the occurrence of the preferred orientation of (002) during mechanical rolling for the formation of the pTi. In addition, an overlap of the peak positions between (002) in the $\alpha$ phase and (110) in the $\beta$ phase exists. The overlap may be caused by the incorporation of Fe as a $\beta$-stabilizer in pTi samples, but the possibility of the existence of this (110) peak in $\beta$ phase was removed by the EDS analysis which did not detect any Fe. According to Peng et al., they also observed this preferred orientation of (002) before their heat treatments, which indicated that the peak originated from $\alpha$ phase rather than $\beta$ phase [210, 211].

After the heat treatment, there was no appearance of XRD patterns of rutile as seen in Figure 3.8. The XRD data includes both the phase information of the bulk sample and the formed nanowires. Therefore, it is needed to realize the contribution from each region such as the bulk and the formed nanowires. The penetration depth is commonly
used to understand the contribution from each region. The penetration depth for the XRD can be expressed by the following equation [255]

\[ x = \frac{\sin \theta}{2\mu} \cdot \ln \left( \frac{1}{1-G_x} \right) \]  

(3.7)

where \( x \) and \( \mu \) are penetration depth and linear absorption coefficient for x-rays, respectively. \( G_x \) is defined as the ratio of intensity diffracted from a depth \( x \) to that diffracted from the whole sample. If \( G_x \) is calculated as 0.90, it means that 90% of the measured intensity of XRD is originated from diffraction from the surface to the depth \( x \). Subsequently, if the penetration depth is known, the contribution of intensity from each region can be calculated by using equation (3.7).

The linear absorption coefficient of Ti, \( \mu_{Ti} \), for Cu K\(_\alpha\) was calculated by using mass absorption coefficient and density of Ti [255], and produced a value of 912.8 cm\(^{-1}\). The length of nanowire was in the range of 100 to 300 nm. It is assumed that the penetration depth for the sample is around 1 \( \mu \)m and within this depth the contribution of XRD intensity is attributed to the nanowire-formed region, oxide layer underneath nanowires and the bulk of pTi sample, respectively. By substituting \( x \) with 1 \( \mu \)m in equation (3.7), the contribution of the bulk to the intensity of the 101 peak (\( 2\theta = 40.2^\circ \)), which is the highest intensity among \( \alpha \)-Ti peaks can be calculated as follows

\[ G_x = 1 - \exp \left( -\frac{2x\mu}{\sin \theta} \right) = 1 - \exp \left( -\frac{1}{2\times10^{-4} cm \times 912.8 cm^{-1} / \sin 20.1^\circ} \right) = 0.41 \]
Hence, 41% of the diffraction intensity of \( \alpha \)-Ti (101) peak was originated within 1 \( \mu \)m depth from the surface. The linear absorption coefficients for TiO, Ti\(_2\)O\(_3\) and TiO\(_2\) are 830, 637 and 530 cm\(^{-1}\), respectively. The contributions for each oxide for its highest intensity peak (002 for TiO, 116 for Ti\(_2\)O\(_3\) and 111 for TiO\(_2\)) were calculated and the values were 0.36, 0.24 and 0.36, respectively. It is worth noting that the peak of each oxide should be shown in the XRD pattern if they exist because the contribution of each oxide is very similar to that of \( \alpha \)-Ti sample. However, there were no peaks of any titanium oxides except the bulk peaks of the sample.

A similar XRD pattern observation was also reported by Peng et al. [210, 211]. In the reports, it was found that there were peaks only from the bulk when pTi was heat treated at 650 \( ^\circ \)C under an aceton atmosphere even though there were shorter nanowires or seeds from SEM observation. This disappearance of XRD peaks of titanium oxides may be explained by considering two possibilities. First, there were no crystalline phases of any oxides. Second, the size of particles and volumetric contribution of any oxides to XRD pattern after the heat treatment is too small to produce detectable intensities. Subsequently, it was suggested to use TEM for the characterization of nanowires from pTi sample. Figure 3.9A shows a high resolution TEM image of an individual nanowire. The diameter of the nanowire was estimated to be approximately 15 nm which was in the range observed under SEM. To identify the phase of the nanowire, a nano-diffraction pattern was obtained on the nanowire and the resultant image is shown in Figure 3.9B. The diffraction pattern revealed that the nanowire is the rutile phase. The zone axis for the diffraction pattern was identified as [0-20]. No peaks other than Ti by EDS were
observed as shown in Figure 3.9C, which indicated that the growth of nanowires on pTi samples were not occurred by the existence of a catalyst.

### 3.3.4 Characterizations of nanowires obtained from Ti alloys

The characterization of heat treated samples to identify the phase of nanowires are much complicated for Ti alloys compared to pTi samples. When Ti alloys are exposed to an environment containing oxidizing gases, there would be the chance of the formation of other oxides due to the existence of alloying elements. For example, there are reports about the formation of alternating layers of Al₂O₃ and TiO₂ after oxidation of Ti64 at an elevated temperature even though the activity of aluminum was very small [256]. The chemical reaction for the formation of Al₂O₃ [254] can be expressed as

\[
2\text{Al (s)} + \frac{3}{2} \text{O}_2 (g) = \text{Al}_2\text{O}_3 (s), \Delta G^{\circ}_{973K} = -1346.0 \text{ kJ/mol.} \tag{3.8}
\]

Even though there are no reports on the formation of vanadium oxides from the oxidation of Ti64 [257, 258], the formation of vanadium oxides would be thermodynamically possible

\[
\text{V (s)} + \frac{1}{2} \text{O}_2 (g) = \text{VO (s)}, \Delta G^{\circ}_{973K} = -730.8 \text{ kJ/mol} \tag{3.9}
\]

\[
4\text{VO (s)} + \text{O}_2 (g) = 2\text{V}_2\text{O}_3 (s), \Delta G^{\circ}_{973K} = -568.1 \text{ kJ/mol} \tag{3.10}
\]

\[
2\text{V}_2\text{O}_3 (s) + \text{O}_2 (g) = 4\text{VO}_2 (s), \Delta G^{\circ}_{973K} = -293.2 \text{ kJ/mol} \tag{3.11}
\]

\[
4\text{VO}_2 (s) + \text{O}_2 (g) = 2\text{V}_2\text{O}_5 (s), \Delta G^{\circ}_{973K} = -84.0 \text{ kJ/mol.} \tag{3.12}
\]

Assuming that there is 1 mole of oxygen gas to compare the free energy of formation of each oxide, the free energies of possible oxides from oxidation of Ti64 is represented in Figure 3.10 as a function of temperature. It was realized that the formation of TiO oxide
was mostly favored thermodynamically and the least favored oxide formation was V$_2$O$_5$.

The Gibbs free energy for the chemical reaction (3.8) can be expressed by

$$
\Delta G_{(3.8)} = \Delta G_{(3.8)}^\circ + RT \ln \frac{a_{Al_{2}O_{3}}}{a_{Al}^2 a_{P_{O_{2}}}^{3/2}}
$$

(3.13)

For pure Al, the activity for Al is unity, but in Ti64 the activity of Al is not unity. The activity value for Al in Ti alloys was reported value is 0.0001 [256]. Considering that the partial pressure in the quartz tube is still high enough to oxidize alloy samples, the chemical reaction (3.8) also proceeds forward. Assuming that the activity of Al$_2$O$_3$ is unity and if the reported value of the activity of Al is used, the Gibbs free energy is calculated by equation (3.13) to be -260.78 kJ/mol. The Gibbs free energies for the formation of TiO, Ti$_2$O$_3$ and TiO$_2$ were also calculated and the values were -37, -74 and -112 kJ/mol, respectively. Therefore, the formation of Al$_2$O$_3$ is still possible even though the activity of Al is very small.

The XRD patterns were obtained on polished Ti64 samples before and after the heat treatment at 700 °C for 8 hours at a flow rate 1000 ml/min of Ar gas. The resultant peaks are represented in Figure 3.11. The XRD pattern of bare polished sample matched the peaks from α and β phases. There were relatively strong α peaks in the XRD pattern. It was found that the strongest peak (110) among β-peaks overlapped with the peak position (002) of α-Ti peak as shown in Figure 3.11. Because of this overlap, it was difficult to determine the relative amount of each phase. The intensity solely originated from the existence of the α phase can be expressed by the following equation [255]

$$
I_{\alpha} = \frac{K_2 R_a C_a}{2 \mu_{\alpha}}
$$

(3.14)
where $K_2$ is a constant and $R_\alpha$ is a constant which depends on $\theta$ and $hkl$ and $C_\alpha$ is the composition of the $\alpha$ phase and $\mu_m$ is the mass absorption coefficient. Similarly, the intensity of $I_\beta$ from $\beta$ phase is also expressed by

$$I_\beta = \frac{K_2 R_\beta C_\beta}{2 \mu_m}$$

(3.15)

The ratio of the intensity of the $\alpha$ phase to the $\beta$ phase is expressed by

$$\frac{I_\alpha}{I_\beta} = \frac{R_\alpha C_\alpha}{R_\beta C_\beta}$$

(3.16)

Therefore, if the ratio of the intensity the $\alpha$ phase to the $\beta$ phase is known, the amount of each phase can be determined. However, there were no other peaks for $\beta$ phase except (110) peak which overlapped with the $\alpha$-phase. Therefore, the relative amount of the $\beta$-phase could not be determined.

After the heat treatment, there were the formation of nanowires but there were no significant peaks from the formation of oxides as shown in the XRD pattern. The most strongest peak of rutile (110) appeared at $2\theta = 27^\circ$, but the relative intensity of rutile peak compared to the peaks of the bulk was very small. It is worth noting that there were position shifts of the peaks of Ti samples before and after the heat treatment. These shifts were originated from the change of the lattice parameter of $c$ rather than $a$ from the $\alpha$ phase Ti. It is believed that the expansion of the lattice parameter $c$ was caused by the incorporation of oxygen into the lattice [222, 253].

Individual nanowires were characterized by TEM to obtain more accurate phase information on nanowires. **Figure 3.12A** shows two individual nanowire images under
TEM. The diameter of nanowires was in the range of 20 to 30 nm. The nanowire located at the bottom showed different contrast based on thickness variation along the length of the nanowire. A high resolution image of an individual nanowire is also shown in Figure 3.12B. The distance between the lattice points matches an interplanar spacing value of (001) of rutile. The growth direction of the nanowire was determined to be [001]. The nano-diffraction image of the nanowire is presented in Figure 3.12C. The phase of the nanowire was determined to be rutile phase of TiO$_2$ with a zone axis of [200]. It is worth noting that nanowires sometimes showed the existence of an outer layer shown in Figure 3.12D. Although the outer layer phase is not identified, it is a compositionally region bearing Al based on the results of TEM-EDS analyses in Figure 3.12D.

$\beta$-Ti (5-5-5) was also used for the growth of nanowires. There are three $\beta$-stabilizers such as Mo, V and Cr in $\beta$-Ti (5-5-5). Total weight percent of $\beta$-stabilizers is 13.5 wt %. Therefore, the dominant phase in $\beta$-Ti(5-5-5) samples is the $\beta$ phase. The XRD patterns of $\beta$-Ti (5-5-5) samples before and after the heat treatment at 700 $^\circ$C for 8 hours at a flow rate of 1000 ml/min in Ar gas were collected and presented in Figure 3.13. The XRD pattern of a bare polished $\beta$-Ti (5-5-5) sample was similar to that of polished Ti64 sample. The overlapping of (110) peak of $\beta$ phase to (002) peak of $\alpha$ phase also occurred. Even though there would be three possible peaks for $\beta$-Ti such as (110), (200) and (211) from $2\theta$ = 20° to 70°, there were no other peaks except (110) of $\beta$ phase, which also caused the difficulty of phase quantification. After the heat treatment, there were also peak position shifts of $\alpha$ phase peaks, which indicated the formation of Ti and oxygen solid solution.
Individual nanowires were collected on a TEM-Cu grid for TEM analyses and the images are presented in Figure 3.14. Bundle of nanowires are shown in Figure 3.14A. The length of nanowires is in the range of 0.1 to 0.8 μm which was shorter than the length observed under SEM. It was believed that the nanowires was broken during TEM sample preparations. Figure 3.14B shows that the average diameter is approximately 30 nm. It is interesting to note that a nanowire at the right corner shows a contrast between an inner layer and an outer layer. The nano-diffraction pattern was taken to determine the phase of nanowires, but it was difficult to analyze because of the overlap of diffraction patterns caused by both the inner layer and outer layer. As shown in Figure 3.14C, there are a lot of diffraction spots and it is difficult to distinguish spots of one phase from the other. Instead of using the diffraction pattern for phase identification, a ring pattern for bundle of nanowires was collected to identify the phase of nanowires. The ring pattern is shown in Figure 3.14D. The distance between the center and a spot was used to match (hkl) of a phase. The camera length, L, was given as 770 mm and the wavelength of electron at 200 kV can be calculated by [259]

\[ \lambda = \frac{h}{[2m_0eV(1+\frac{eV}{2m_0c^2})]^\frac{1}{2}} \]  

where \( m_0, \) c and \( h \) are the electron mass, the speed of light and Planck’s constant, respectively. The calculated value of \( \lambda \) at 200 kV is 0.00251 nm. The calculated distance, \( r \), between the center and a spot representing (hkl) can be calculated by [259]

\[ L\lambda = rd \]
where \(d\) is the interplanar spacing of (hkl). **Table 3.1** summarizes calculated \(r\) values for each (hkl) for both rutile and anatase of TiO\(_2\). Comparing these values in **Table 3.1** to measured values represented in **Table 3.2**, it was concluded that the phase of bundle of nanowires is rutile.

Based on reported literature [210, 211], the growth of nanowires is believed to be by metal oxidation process. To confirm the growth of nanowires by metal oxidation process, a TGA experiment on a \(\beta\)-Ti (5-5-5) sample was performed. If the growth of nanowires was established by metal oxidation, there would be weight gain due to the formation of oxide. If the process for the growth of nanowire is associated with the evaporation or gas phase etching reported by Yoo et al. [260], the weight change for the process would be shown to decrease as the duration of the TGA experiment increase. The weight change percent from TGA experiment is shown in **Figure 3.15**. Even though there are fluctuations in the weight change, the trend is shown to increase, which indicates that the process for the growth of nanowires is by metal oxidation. The reason for the fluctuation is believed to be related with the resolution of the TGA equipment. Assuming that the diameter of nanowire is 30 nm and the growth rate of nanowire is 1 nm/sec with the density of nanowire, 100 wires/\(\mu\)m\(^2\), the weight change rate can be calculated by obtaining the volume change rate. Because the surface area of the sample is 0.000025 m\(^2\), the rate of volume increase is \(1.78 \times 10^{-9}\) cm\(^3\)/sec and then the weight change rate is \(7.97 \times 10^{-9}\) g/sec which is beyond the resolution of the TGA equipment, \(10^{-5}\) to \(10^{-6}\) g/sec. Therefore, it is suggested that the weight change of the sample is monitored by a high resolution TGA equipment. With results from higher resolution TGA, the diffusivity for
the growth of nanowires may be extracted, thus leading to a better understanding of the oxidation process.

### 3.4 Conclusions

The growth of nanowires on pTi, Ti64 and β-Ti was observed. The diameter of nanowires is in the range of 20 to 60 nm for all the samples. The length of nanowires for pTi is less than 500 nm and this length is the shortest among nanowires from all the samples. For both Ti64 and β-Ti samples, the length of nanowires ranged from 2 to 5 μm. The diameter of nanowires was confirmed by TEM analyses. From XRD pattern analyses, there was no detection of rutile phase even though there was the existence of the most strongest peak (110) of rutile phase for both Ti64 and β-Ti but the intensity of the peak was very small. To identify the phase of nanowires, the images of SAED for all the samples were taken. Based on the SAED patterns except that for β-Ti, all the nanowires were determined to be rutile phase of TiO₂. The SAED pattern of β-Ti was very complicated due to many spots originating from two phases. Instead of using the SAED pattern, the ring pattern on the bundle of nanowires was collected to determine the phase. With the results of the ring pattern, the phase of the bundle of nanowires was determined as the rutile phase of TiO₂. The nanowires from Ti alloy samples sometimes showed the existence of an outer layer which was Al rich region compositionally.
Figure 3.1 A schematic diagram of the equipment set up.
Figure 3.2 Surface images of A: polished pure Ti samples before a heat treatment, B: pure Ti samples heat treated at 600 °C for 8 hours at the flow rate, 200 ml/min and C: at a high magnification.
Figure 3.2: Continued
Figure 3.3 Surface images of pure Ti after heat treatments at 900 °C for 1 hour and B shows an image at a high magnification.
Figure 3.4 Surface images of Ti64 samples after heat treatments at 700 °C for 8 hours at the flow rate of 1000 ml/min and B shows the image at a high magnification.
Figure 3.5 Surface images of A: etched Ti64 samples, B: Ti64 samples after heat treatments at 700 °C for 2 hours at the flow rate of 1000 ml/min and C: at a high magnification.
Figure 3.5: Continued
Figure 3.6 Titanium self diffusion and various alloying elements in β and α phase as a function of temperature and dashed line is the transition temperature from β to α phase [218].
Figure 3.7 Surface images of β-Ti (5-5-5) samples; A: polished samples, B: samples after heat treatments at 700 °C for 8 hours at the flow rate of 1000 ml/min and C: at a high magnification.
Figure 3.7: Continued
Figure 3.8 XRD patterns of pure Ti samples before and after heat treatments at 600 °C for 8 hours at the flow rate of 200 ml/min.
Figure 3.9 A: TEM image of nanowires showing the diameter and length of nanowires, B: the nano-diffraction pattern showing the rutile phase of TiO$_2$ and C: the EDS pattern of a TiO$_2$ nanowire showing that there are no impurities.
Figure 3.9: Continued
Figure 3.10 The Gibbs formation energies per mole of O$_2$ of possible oxides from oxidation of pure Ti and other metals as a function of temperature.
Figure 3.11 XRD patterns of Ti64 samples before and after heat treatments at 700 °C for 8 hours at the flow rate of 1000 ml/min.
Figure 3.12 A: TEM image showing two nanowires, and B: the lattice image of a nanowire shown in A, indicating the growth direction [001], C: the nano-diffraction pattern of the nanowire showing the rutile phase of TiO$_2$ and D: EDS data showing an outer layer bearing Al.
Figure 3.12: Continued
Figure 3.13 XRD patterns of polished β-Ti samples before and after the heat treatment at 700 °C for 8 hours at the flow rate of 1000 ml/min.
Figure 3.14 A: TEM image showing bundle of nanowires, B: TEM image showing the contrast, indicating the existence of two layers, C: the nano-diffraction pattern showing a lot of spot caused by two layers and D: a ring diffraction pattern obtained from the bundle of nanowires, indicating that there is rutile phase.

Continued
Figure 3.14: Continued
Figure 3.15 Isothermal TGA data of $\beta$-Ti sample for 6 hours.
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<th>(hkl)</th>
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<th>d(hkl) TiO$_2$ anatase /nm</th>
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Table 3.1 Calculated r values for each (hkl) of rutile and anatase of TiO$_2$. 
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<th>(hkl)</th>
<th>d(hkl) Al₂O₃ almina /nm</th>
<th>Calculated value /mm</th>
<th>Calculated value /mm</th>
<th>Measured r values</th>
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**Table 3.2** Calculated r values of corundum Al₂O₃ and rutile TiO₂ and measured r values.
CHAPTER 4

PROCESS OPTIMIZATION

4.1 Introduction

The growth of nanowires on three different Ti alloy samples after heat treatments at 600 or 700 °C for 8 hours was observed. The process for the growth is a simple and low cost method, which produces pure TiO$_2$ rutile nanowires or inner core rutile covered by an outer layer bearing Al. The growth is believed to be caused by oxidation of pure Ti or Ti alloys under a flowing Ar gas environment containing a low oxygen concentration, approximately 500 ppm. The growth of nanowires by oxidation of metals will be beneficial in that the method does not require any catalysts and high temperature for thermal evaporation to generate vapor species and has high scalability and reproducibility.

Controlling parameters for the process are temperature, flow rate, chemical composition of Ti alloy samples, and gas environment. The morphology of the surface can be affected by these parameters. At first, the change of the morphology on pure Ti and Ti alloys is discussed depending on temperature and flow rate. The growth of nanowires was accelerated on the β-phase as observed in chapter 3. In order to elucidate
the effects of β-phase and alloying elements, different Ti alloys with various chemical compositions are used.

It is also required to improve the growth of nanostructures on pure Ti samples because they are inexpensive and easy to obtain. It is also realized that the selectivity between pure TiO₂ rutile nanostructures and rutile covered by the outer layer is to open up utilization of each nanostructure depending on specific applications. It is known that the growth of whiskers or nanowires is improved by incorporation of water vapor [261]. Therefore, the effect of water vapor was studied by bubbling Ar through a water bath at room temperature. Moreover, surface treatment effects on the growth of nanowires was investigated by etching and pre-annealing treatments on β-Ti (5-5-5) samples.

4.2 Experimental

4.2.1 Sample preparation

Additional Ti6 (Ti-6 wt % Al), Ti-Mo (Ti-18 wt % Mo), Ti-V (Ti – 10 wt % V) and Ti685 (Ti-6.85 wt % Al 1.6 wt % V) along with three Ti alloy samples such as pure Ti, Ti64 and β-Ti(5-5-5) were used for experiments. The source of the alloy samples is summarized in Table 4.1. Samples for heat treatments were prepared by the same manner as described in chapter 3. Three different Ar gas flow rates such as 200, 500 and 1000 ml/min were used to check the effect of the flow rate on the morphology change on pure Ti, Ti64 and β-Ti samples. Various heat treatment temperatures such as 600, 700, 800, and 900 °C were used to observe the morphology changes on pure Ti, Ti64 and on β-Ti samples. 1 and 3 % O₂ in Ar gas were prepared by mixing the Ar gas with pure O₂ gas to
check the effects of the oxygen amount on the growth of nanowires on Ti64 samples. The mixture of the Ar gas with water vapor was generated by bubbling the Ar gas through a glass flask containing DI water during heat treatments. The generated gas mixture was carried into the tube. During the heat treatment, the humidity level was monitored by a humidity sensor (HMP234, Vaisala) and the relative humidity was always greater than 80%.

β-Ti (5-5-5) samples were annealed in 5 % H₂ balanced Ar gas at 900 °C for 3 hours to remove α-phase because β-phase is stable at 900 °C. After that, mechanical polishing was performed and chemical etching was followed by using Kroll’s solution to remove the highly deformed layer created by polishing.

4.2.2 Materials Characterization

The surface morphologies of pure Ti and Ti alloy samples after heat treatments were observed by a high resolution field emission scanning electron microscope (FE-SEM, Model Sirion, FEI). The samples were coated with Au thin film before SEM observations to prohibit electron charging effect.

The phase of the Ti alloy samples before and after heat treatments was determined by using a X-ray diffractometer (Model XDS-2000, Scintag) using Cu Kα radiation. After the growth of nanowhiskers after the heat treatment of pure Ti samples at 700 °C for 8 hours in the mixture of Ar with water vapor at the flow rate of 1000 ml/min, nanowhiskers were collected by the method described in chapter 3. These were characterized by a high resolution transmission electron microscope (HRTEM, Model Tecnai TF20, FEI).
4.3 Results and Discussion

4.3.1 Optimization of processing condition for the growth of nanowires

Heat treatment temperature and flow rate of the Ar gas

Pure Ti samples

Exposure of pure Ti substrates to Ar gas containing a low concentration of oxygen at a flow rate of 200 ml/min for 8 hours at 600 °C resulted in the growth of TiO$_2$ nanowires as presented in Figure 3.2B and C. In order to observe the effects of the flow rate on the growth of nanowires, two flow rates were used, 500 ml/min and 1000 ml/min. The surface morphology of the two samples are presented in Figure 4.1. There were a few nanowires with fine nanocrystals less than 100 nm in size for the flow rate of 500 ml/min in Figure 4.1A. For the flow rate of 1000 ml/min, there were no nanowires but only nanocrystals. The effect of the flow rate was more obvious as the temperature for the heat treatment increased. For the results of heat treatments at 700 °C at three different flow rates, separated and extruding crystals were formed at the lowest flow rate as shown in Figure 4.2A. The longest extruding crystal having approximately 500 nm in length is seen in Figure 4.2B and typical extruding crystals were shorter. These separated and extruding crystals disappeared and connected to each other at the highest flow rate. At the intermediate flow rate, 500 ml/min, extruding crystals existed together with fine crystals, but the density of extruding crystals was low. At the highest heat treatment temperature, 800 °C, the size of crystals increased up to 1 μm and most crystals were well faceted except some platelets for the lowest flow rate. There were gaps between crystals for the
lowest flow rate and as the flow rate increased the gaps disappeared as shown in Figure 4.3D. Well faceted crystals seemed to be connected and form continuous oxide scale at the highest flow rate. Figure 4.4 shows a schematic diagram of the processing map with resultant structures. It can be concluded that the processing window for the growth of nanowires on pure Ti is narrow.

The XRD patterns of the samples heat treated at 600 °C are shown in Figure 4.5A. The strongest peak of rutile (110) was observed for both flow rates, 500 and 1000 ml/min. Based on the ratio of the strongest peak of rutile to the peak of Ti, the thickness of TiO₂ oxide layer is expected to be very thin. As the heat treatment temperature increases, the intensity of the strongest peak of rutile increases indicating the increase in the oxide thickness as shown in Figure 4.5B and C.

**Ti64 and β-Ti(5-5-5) samples**

Figure 4.6 shows the surface morphologies of Ti64 samples after heat treatments with an Ar flow rate of 1000 ml/min at 600, 800, and 900 °C. The surface morphology of Ti64 samples at 700 °C is shown in Figure 3.4A and B. At first, shorter nanowires less than 500 nm in length were observed from the lowest heat treatment temperature. Some of the surface were not covered by shorter nanowires, which indicated that there was the growth rate difference depending on the region of the surface as seen in Figure 4.6A. The surface image for the flow rate of 1500 ml/min is shown in Figure 4.6B. The length of nanowires seems to be constant compared to that of nanowires for the flow rate of 1000 ml/min but the density of nanowires decreased. A region which is not covered by nanowires showed fine crystals less than 200 nm in size. When the heat treatment
temperature was increased to 800 °C, a mixture of well faceted crystals with nanowires was observed in Figure 4.6C. The length of nanowires was in the range of 0.5 to 2 μm. Well faceted crystals were observed and connected to each other at the highest heat treatment temperature and no nanowires were observed.

Except for the XRD peak patterns of Ti64 samples heat treated at 600 °C, all the peak patterns show the rutile phase of TiO₂ as shown in Figure 4.7. As the heat treatment temperature increased, the intensity of the strongest peak (110) became stronger, which indicated the increase in the oxide thickness and crystalinity. The disappearance of the rutile peaks in the XRD pattern of the sample heat treated at 600 °C was caused by the fact that there was not enough shorter rutile nanowires to create the intensity detected by the XRD.

The growth of nanowires on a β-Ti(5-5-5) sample after a heat treatment at 700 °C for 8 hours at an Ar flow rate of 200 ml/min was observed. The length of nanowires ranged from 0.7 to 3.3 μm as shown in Figure 4.8. The diameter of nanowires seems to be constant as the diameters of nanowires grown from pure Ti and Ti64 samples. The growth of nanowires on β-Ti(5-5-5) at a flow rate of 1000 ml/min is shown in Figure 3.6B and C. The effect of the change of the flow rate from 1000 ml/min to 200 ml/min on the length and the density of nanowires grown on β-Ti samples was not noticed. β-Ti (5-5-5) samples were exposed at a fixed flow rate, 1000 ml/min for 8 hours at three different temperatures, 600, 800 and 900 °C. Figure 4.9 shows the morphologies of the surfaces of each sample. The trend of the morphology changes was similar to those of Ti64 as the heat treatment temperature changed. At the lowest heat treatment temperature, shorter
nanowires were formed all over the surface. The length of the nanowires was approximately 100 nm. As the heat treatment temperature increased, a mixture of well faceted crystals with a few nanowires were observed and then only well faceted crystals were observed at the highest heat treatment temperature. Figure 4.10 shows a schematic diagram of the processing map with resultant structures for both Ti alloys. It is worth noting that the growth of nanowires on Ti64 and β-Ti(5-5-5) samples is generous in terms of the flow rate compared to pure Ti because the growth of nanowires on pure Ti was only allowed at the lowest flow rate of 200 ml/min, but the growth of nanowires on both alloy samples were possible even at the highest flow rate (1000 and 1500 ml/min). It is not yet understood why the growth of nanowires on alloy samples is possible within a wide range of the flow rate at this point.

Another question from various heat treatment temperature experiments is how a transition from nanowires to well faceted crystals occurs. A systematic heat treatment temperature change using a more narrow interval compared to 100 °C step should be performed in the future to obtain additional information about the transition. For the effects of the heat treatment temperature on the morphology changes, as the temperature increases, the rate of interactions between Ti and oxygen is increased, which causes the formation of bigger and well faceted crystals. Consequently, the growth of nanowires on both pure Ti and Ti alloy samples was maximized at 600 and 700 °C, respectively.

Even though the relation of nanowire formation with the Ar gas flow rate is not clear on Ti alloy samples, the dependence of the growth of nanowires from pure Ti on the flow rate implies that the growth of nanowires is at least partially affected by the
diffusion of the reactant gas through a gaseous boundary layer. A schematic diagram of
the gas transport process during oxidation is represented in Figure 4.11A. When gas
flows over a Ti or Ti alloy plate, viscous drag between the sample and the gas creates the
gaseous boundary layer. O₂ gas diffuses in the gaseous boundary layer. Even though the
diffusion coefficient of O₂ gas is 0.203 cm²/sec at 70 °C [262], which indicates that the
diffusion of O₂ gas would not be limited, the report by Yoo et al. [186] indicated that the
diffusion of H₂ and H₂O in the gaseous boundary layer was limited by the gaseous layer
thickness. While Chen et al. did not mention the relation of the flow rate with the gaseous
layer thickness, they reported that the growth Si-C-N composite nanowires was only
observed below the flow rate of 40 sccm [244]. The morphology of the surface was
suddenly changed to micro/nanocrystals from nanowires when the flow rate was over 50
sccm, which indicates that the flow rate of the gas plays role in dictating the morphology
of the structure.

The thickness of the gaseous boundary layer, δ, can be calculated but it is
required to determine a pattern of the gas flow by using the Reynolds number before
calculating the thickness, δ. The Reynolds number, Re, can be used to determine whether
the pattern of the gas flow is laminar or turbulent. The Reynolds number, Re, for the Ar
gas flow can be calculated by [263]

\[
Re = \frac{Dv\rho}{\eta}
\]  

(4.1)

where, D is the tube diameter and \(v\) is the average velocity of gas (volumetric gas flow
rate divided by cross-sectional area), and \(\rho\) and \(\eta\) are the density and viscosity of gas,
respectively. The Reynolds number for the transition from laminar to turbulent flow is
2100. Substituting the diameter of the tube, 0.0254 m, \( v = 0.033 \text{ m/s} \), \( \rho = 0.5 \text{ kg/m}^3 \) and \( \eta = 4.18 \times 10^{-5} \text{ kg/m} \cdot \text{s} \) for Ar gas at 973 K into the equation (4.1), the Reynolds number is
19.98 which indicates that the gas flow in the tube follows laminar flow because the
Reynolds number is much lower than 2100. The layer thickness, \( \delta \) [263] is expressed by,
\[
\delta = 5.0 \left( \frac{v}{v_\infty} \right)^{\frac{1}{5}} x^{\frac{1}{2}}
\]
where, \( v \) is the kinematic viscosity, \( v_\infty \) is the velocity of gas flow, and \( x \) is the distance
from the leading edge of the sample. It is realized that the gaseous boundary layer
thickness, \( \delta \), decreases as the Ar gas flow rate increases. Figure 4.11B shows the plot of
the gaseous boundary layer thickness (\( \delta \)) as a function of the distance (\( x \)), defined as the
distance from a leading edge of the sample, when the Ar gas flow rate is 200, 500 and
1000 ml/min. Assuming that the length of a sample is 0.005 m (sample thickness), \( \delta \) for
the flow rate 200 ml/min is 0.020 m at the center of the sample (\( x = 0.0025 \text{ m} \)) while \( \delta \)
for the flow rate of 1000 ml/min is 0.0089 m. Therefore, it is realized that the transport
process of \( \text{O}_2 \) through the boundary layer for the flow rate of 200 ml/min is more difficult
than that for the flow rate of 1000 ml/min, thus resulting in the growth of nanowires
rather than the formation of continuous oxide layer. Kwon [243] reported that the flow
rate can determine whether the growth is isotropic or anisotropic. According to his model,
anisotropic growth is preferred at lower flow rate to higher flow rate.

A relatively low Ar flow rate is required to accomplish longer nanowires at a high
density since the gas flow rate affects transport of \( \text{O}_2 \). In order to clarify transport process
of O₂, careful TGA experiments should be performed in the future. If transport process through gaseous boundary layer or reaction at the surface is the rate limiting step, a linear rate law is generally observed [264].

**Chemical composition and phase of samples**

It was found that the growth of nanowires was preferred on the β phase. β phase can be synthesized by addition of β stabilizers such as V, Mo and Cr, thus resulting in β phase with different chemical compositions. Therefore, it is necessary to elucidate the effect of β stabilizer on the growth of nanowires. At first, Ti18Mo (Ti-18 wt % Mo) was used to check the growth of nanowires at 700 °C for 8 hours with a Ar flow rate of 500 ml/min. The morphology of the surface is presented in Figure 4.12. While nanowires were observed at a low density in a small area, the dominant surface structure was continuous oxide scale. Each crystal was well faceted and less than 1 μm in size. A binary alloy, TiV (Ti- 10 wt% V) was also investigated to determine the effects of V on the growth of nanowires in the β phase. No nanowires were observed and the morphology was continuous oxide scale as shown in Figure 4.12C and D. A different commercial β-Ti (Ti- 12 wt% Mo-6 wt% Zr-4.5 wt% Sn) without V or Al was used to confirm that Mo did not play any role in generating the growth of nanowires. The heat treatment conditions were the same as for the previous samples. No nanowires were detected and the surface morphology was continuous oxide layer as shown in Figure 4.13. Consequently, it is concluded that V or Mo does not play any roles in producing nanowires from these experiments. It is also concluded that β phase does not guarantee
the growth of nanowires, but some other factors should be considered for the growth of nanowires. It was realized that there was always Al in alloy samples whenever the growth of nanowires was accomplished. Therefore, Ti6 (Ti-6 wt % Al) was used to check the effect of Al on the growth of nanowires in the α phase. The same heat treatment condition was used and the resultant morphology of the surface is presented in Figure 4.14. While the growth of nanowires from pure Ti at the same condition did not produce any nanowires, there were a few nanowires grown on a Ti6 sample. It was found that there was a fork shape of nanowires as seen in Figure 4.14B. Li et al. [265] reported that certain amount of TiO2 twinned crystals like nanoforks were formed along with straight and rod-like whiskers by microemulsion growth methods. Depending on the angle between two nanowires, they presented that there were two kinds of twinned whiskers. The angles were 55 and 114°, respectively. Each nanowire or whisker had a common [010] direction. They found that there was a dislocation embedded in the interior of the twinned whisker, which indicated that the growth of nanoforks was caused by the existence of a dislocation. Our nanoforks are similar to the reported ones. These nanoforks were observed only from Ti6 samples. In the future, roles of Al should be clarified by identifying the existence of twins and dislocations via HRTEM analyses.

The microstructure of Ti alloys can be altered by a heat treatment process chosen. Matt created such samples of composition Ti-6.85 wt% Al-1.6 wt% V with a specific microstructure schematically shown in Figure 4.15A. The interesting feature of the microstructure of these samples is that the β phase exists only along the grain boundaries of the α phase. The dominant phase is α-phase and the amount of β phase is relatively
small, thus resulting in distinctive differences between $\alpha$ and $\beta$ phase. The heat treatment conditions were the same as the previous samples. There were long nanowires at a high density on sparse regions located along the grain boundary, indicating that these long nanowires were grown on the $\beta$ phase. The length of nanowires was in the range of 2 to 5 $\mu$m. Shorter nanowires at a high density were observed between long nanowires grown regions. It was found that the density and length of nanowires were better than those of nanowires grown on pure Ti prepared by the same heat treatment conditions. These experimental results indicated that Al alloying element was required for successful growth of nanowires even in $\beta$ Ti alloys. The exact role of Al is not understood very well at this point.

**Effects of gas atmosphere on the growth of nanowires**

**Amount of oxygen in the gas phase**

The growth of nanowires was observed so far under the flow of Ar gas containing a low concentration of oxygen, approximately 500 ppm. The morphology changes caused by different oxygen concentrations in the Ar gas were explored. Figure 4.16 shows the morphologies of the surface of Ti64 samples using two different oxygen concentrations, 1% and 3 % O$_2$ at 700 °C for 8 hours at the flow rate of 1000 ml/min. There were fine and spherical crystals in some regions for 1 % O$_2$. For 3 % O$_2$, Figure 4.16B shows the morphology of the surface is a typical oxide scale from an oxidation process. No nanowires were observed on both samples, indicating that the growth of nanowires was only achieved under the Ar flowing gas containing a lower oxygen concentration. This
result also indicates that the growth mode is determined by the transport or supply of oxygen. As the oxygen concentration increases, the supply of oxygen increases, thus resulting in continuous oxide scale which was deduced from the model proposed by Kwon [243].

**Water vapor heat treatments of pure Ti and Ti64 samples**

A mixture of Ar with water vapor was introduced to check the effects of water vapor on the growth and morphology of nanowires. Figure 4.17A shows the surface morphology changes on pure Ti after heat treatments at 700 °C for 8 hours at the flow rate of the mixture of 1000 ml/min. There is a certain amount of nanobelts along with nanowhiskers. The cross-sectional image of an edge of the sample clearly shows that the length of nanowhiskers or nanobelts is in the range of 5 to 30 μm. It is realized that the growth rate of nanowhiskers or nanobelts was drastically enhanced by the incorporation of water vapor. It is worth noting that as shown in Figure 4.17C the growth of nanowhiskers starts on the base of the oxide having a shape of a wedge and then they grow and the width of whiskers tapers as the length of nanowhiskers increases. Figure 4.17D shows the morphology of the surface of a sample prepared by the same heat treatment conditions except the flow rate, 200 ml/min. As the flow rate was decreased, it seemed that the amount of nanobelts decreased and nanowires increased. Figure 4.18 shows a TEM image of individual nanowhisker. The widths of the whiskers at the base and the tip is approximately 330 and 100 nm, respectively. The SAED pattern was collected on the whisker to determine the phase of the whisker. From the SAED pattern
shown in Figure 4.18B, the phase of the whisker is rutile TiO₂ and the zone axis for the
diffraction pattern was [-111].

The effects of water vapor on the morphology change and growth of
nanostructures by using Ti64 samples were also observed. The heat treatment conditions
for Ti64 samples were the same as those for pure Ti samples. Figure 4.19A and B shows
the morphology changes of samples at a flow rate of 1000 ml/min. Rectangular shape
bars were formed all over the surface and some of the bars were stacked on others. It was
realized that the aspect ratio of rectangular bars was small and an estimated value from
the longest bar was approximately 4, which was smaller than 100 obtained from
nanowires grown from Ti64 samples. As the flow rate was decreased from 1000 to 200
ml/min, the changes of the surface morphology are represented in Figure 4.19C and D.
One difference between two different flow rate experiments is the density of bars. The
density of bars was reduced at the lower flow rate and there were mounds of oxide
crystals between bars as shown in Figure 4.19D.

Even though there have been reports about the growth of whiskers by heat
treatments under atmospheres containing water vapor [215, 261], the role of water vapor
for 1-D growth is not yet understood. There was a report that described the role of
adsorbed hydroxyl groups as surface diffusion inhibitors [215]. The growth of
nanowhiskers or nanobelts from pure Ti samples is caused by the surface diffusion
limitation which prevents coarsening of oxide nuclei by this model [215]. However, the
role of hydroxyl group as surface diffusion inhibitor is not applicable to explain the
growth of bars from Ti64 samples because of their decreased aspect ratio, which may be
caused by increased surface diffusion. One point noted is that the concentration of oxygen in the heat treatment tube measured by an oxygen sensor increased from 500 to 5000 ppm when the mixture (Ar+H₂O) gas was used. The increased oxygen concentration may play a role in thickening nanowires and transforming nanowires into bars, but the reason that thickening of nanowires for pure Ti samples does not occur under the mixed gas is still unknown.

The other plausible explanation would be the adsorption rate difference among various crystal faces of TiO₂. There are not much differences in terms of adsorption of oxygen on the faces of TiO₂ [241]. However, when the mixture gas is used, if there would be big anisotropic difference, then it would result in the growth of nanostructure in one dimension. For Ti64 samples, the outer layer may play a role in increasing the growth rate in the lateral direction when it interacts with hydroxyl group. However, a question regarding anisotropic difference is that - is it big enough to generate abnormal one dimensional growth? According to Wang et al. [239], one dimensional growth because of anisotropy is possible for ZnO, but it is questionable for other oxides because there are not huge anisotropic differences.

**Effects of the surface state on the growth of nanowires**

A pre-annealing treatment was performed to convert α to β phase at 900 °C for 3 hours. After the heat treatment, the peak pattern of XRD was collected on a pre-annealed sample as seen in Figure 4.20. The peak pattern shows that there are no peaks related to α-phase. While there were regions without nanowires on β-Ti (5-5-5) samples without the pre-annealing treatment after the heat treatment at 700 °C for 8 hours at the flow rate 137
of 500 ml/min, the growth of nanowires on samples having the pre-annealing treatment is widespread, indicating that the growth of nanowires is more uniform as shown in Figure 4.21. Polished β-Ti (5-5-5) samples was etched to remove highly deformed layer to restore the orientation of grains. Figure 4.22 shows the growth of nanowires on an etched sample with the pre-annealing treatment. It is realized that the growth of nanowires is different from grain to grain. Because the intensity of (110) of β-phase is the strongest, most of the grains are (110), but some of them are (200). While nanowires on (110) grains is perpendicular to each other and long and the density of nanowires is high, nanowires on (200) grains is in-plane as shown in Figure 4.22C and the density of nanowires is low.

4.4 Conclusions

As the heat treatment temperature increased, well faceted crystals were formed instead of the growth of nanowires on both pure Ti and alloy samples because of the reaction between Ti and oxygen increased. While the processing window for the growth of nanowires on Ti is narrow, the processing window for Ti alloys is much wider. As the flow rate changed, the surface morphology changed on pure Ti but the growth of nanowires on alloy samples seemed not to be affected. Compared to pure Ti, the growth of nanowires on Ti alloy samples was more generous regarding the flow rate. As the oxygen amount increased, the growth of nanowires on alloy samples was also hindered, which indicated that the growth of nanowires was only allowed under a gas environment containing a low oxygen concentration. As the mixture of gas (Ar + H₂O) was
introduced, the growth of nanowhiskers and nanobelts was promoted on pure Ti sample but there were nanobar formed from Ti64 samples. The growth of nanowires was affected by the surface treatment of samples. Once the orientation of grains was recovered by etching, the direction of nanowires was affected by the orientation of grains. The direction of nanowires on (110) grains was perpendicular to each other, but nanowires on (200) grains were parallel to the surface, indicating an orientation relationship.
<table>
<thead>
<tr>
<th>Material</th>
<th>Composition</th>
<th>Source</th>
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</thead>
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<tr>
<td>Ti6</td>
<td>Ti-6 wt% Al</td>
<td>Matt Brandes</td>
</tr>
<tr>
<td>Ti-Mo</td>
<td>Ti-18 wt% Mo</td>
<td>Rob Williams</td>
</tr>
<tr>
<td>Ti-V</td>
<td>Ti-10 wt% V</td>
<td>Peter Collins</td>
</tr>
<tr>
<td>Ti685</td>
<td>Ti – 6.85 wt% Al - 1.6 wt% V</td>
<td>Matt Brandes</td>
</tr>
<tr>
<td>β-Ti (5-5-5)</td>
<td>Ti – 5 wt% Al, V, Mo-3.5 wt% Cr- 0.5 wt% Fe</td>
<td>Soumya Nag, John Folz</td>
</tr>
</tbody>
</table>

**Table 4.1** Ti alloys and their sources
Figure 4.1 Surface images of the surfaces of pure Ti after heat treatments for 8 hours at 600 °C A: for the flow rate of 500 ml/min and B: the flow rate of 1000 ml/min.
Figure 4.2 The surface images of pure Ti after heat treatments for 8 hours at 700 °C at the flow rates, 200, 500 and 1000 ml/min. A: at a low magnification at the flow rate of 200 ml/min, B: high magnification, the surface images C: at the flow rate of 500 ml/min and D: the flow rate of 1000 ml/min.
Figure 4.2: Continued
Figure 4.3 The surface images of pure Ti after heat treatments for 8 hours at 800 °C at the flow rates of 200, 500 and 1000 ml/min. A: at a low magnification at the flow rate of 200 ml/min, B: high magnification, the surface images C: at the flow rate of 500 ml/min and D: the flow rate of 1000 ml/min.

Continued
Figure 4.3: Continued
Figure 4.4 A schematic processing map with resultant structures on pure Ti.
Figure 4.5 XRD patterns of pure Ti samples after heat treatments A: at 600 °C for the flow rate of 500 and 1000 ml/min, B at 700 °C for three flow rate of 200, 500 and 1000 ml/min and C: at 800 °C for the flow rate of 200, 500 and 1000 ml/min.

Continued
Figure 4.5: Continued

![Graph showing X-ray diffraction patterns at different flow rates (1000 ml/min, 500 ml/min, and 200 ml/min). Peaks labeled (210), (220), (110), and (211) with symbols indicating Rutil, α-Ti, and β-Ti phases.]

Continued
Figure 4.5: Continued
Figure 4.6 The surface images of Ti64 after heat treatments for 8 hours A: at 600 °C with the flow rate of 1000 ml/min, B: at 700 °C with the flow rate 1500 ml/min, C at 800 °C with the flow rate of 1000 ml/min and D: at 900 °C.
Figure 4.6: Continued
Figure 4.7 The XRD peak patterns from Ti64 samples after heat treatments at the flow rate of 1000 ml/min at three different temperatures, 600, 800 and 900 °C.
Figure 4.8 The surface image of a $\beta$-Ti(5-5-5) sample after a heat treatment at 700 °C for 8 hours at an Ar flow rate of 200 ml/min.
Figure 4.9 The surface images of $\beta$-T(5-5-5) samples after heat treatments for 8 hours at the flow rate of 1000 ml/min A: at 600 °C, B: at 800 °C and C: at 900 °C.
Figure 4.9: Continued
Figure 4.10 A schematic processing map with resultant structures for Ti alloys.
Figure 4.11 A: Schematic diagram of the gaseous layer formation and B: the gas layer thickness vs the distance, x, from the edge of the sample at three different flow rates.
Figure 4.12 Surface images of various Ti alloys after the heat treatment at 700 °C for the flow rate of 500 ml/min for 8 hours A: Ti18Mo at a low magnification, B: high magnification, C: TiV at low magnification and D: high magnification.
Figure 4.12: Continued
Figure 4.13 The Surface images of a commercial $\beta$-Ti (Ti- 12 wt% Mo-6 wt% Zr-4.5 wt% Sn) after the heat treatment at 700 °C for the flow rate of 500 ml/min for 8 hours A: at a low magnification and B: high magnification.
Figure 4.14 The surface images of a Ti6 after the heat treatment at 700 °C for the flow rate of 500 ml/min for 8 hours A: at a low magnification and B: high magnification.
Figure 4.15 A: schematic diagram of the microstructure of the sample, B: the surface image of the sample after the heat treatment at 700 °C for the flow rate of 500 ml/min for 8 hours C: a location showing longer nanowires and shorter nanowires and D: shorter nanowires at a high magnification.
Figure 4.15: Continued
Figure 4.16 The surface images of Ti64 samples using two different oxygen concentrations. A: 1% O₂ used for the heat treatment at 700 °C for 8 hours at the flow rate of 1000 ml/min and B: 3% O₂ used.
Figure 4.17 A: the surface image of pure Ti after the heat treatment under the mixture of Ar with water vapor at 700 °C with the flow rate of 1000 ml/min for 8 hours, B: cross sectional image showing the length of nanowires, C: an image showing the base and the growth of nanowire starting from the base and D: the surface image of pure Ti at a lower flow rate of 200 ml/min.

Continued
Figure 4.17: Continued
Figure 4.18 A: TEM image of individual whisker and B: SAED pattern of the whisker showing the phase of rutile.
Figure 4.19 A: the surface image of Ti64 after the heat treatment under the mixture of Ar with water vapor at 700 °C with the flow rate of 1000 ml/min for 8 hours, B: at a high magnification, C: the surface image change at the flow rate of 200 ml/min and D: at a high magnification.
Figure 4.19: Continued
Figure 4.20 A XRD pattern of a sample before and after the pre-annealing treatment.
Figure 4.21 The surface image of the pre-annealed sample after the heat treatment at 700 °C for 8 hours at the flow rate of 500 ml/min, showing that the growth of nanowires is uniform.
Figure 4.22 The surface images of the pre-annealed sample after etching and then followed by the heat treatment at 700 °C for 8 hours at the flow rate of 500 ml/min. A: The growth of nanowires is different from grain to grain, B: the growth of nanowires on (110) grain showing that the directions of nanowires are perpendicular to each other and C: the growth directions of nanowires on (200) grain are parallel to the surface.

Continued
Figure 4.22: Continued
CHAPTER 5

TITANIUM OXIDE NANOWIRE FORMATION - GROWTH MECHANISM

5.1 Introduction

In the previous chapters, the effect of processing parameters such as temperatures, flow rates, and chemical compositions of Ti alloys on the formation of nanowires, as well as the characterizations of nanowires, were discussed. This chapter deals with a possible mechanism of the formation of nanowires. Even though the mechanism is not fully understood, the growth of nanowires based on thermal oxidation under a limited supply of oxygen is proposed and some justifications are provided based on experimental observations.

5.2 Theory

As discussed in the previous chapters, the growth of nanowires was accomplished by heat treatments under a limited supply of oxygen. It is subsequently required to pursue
physical understanding to answer questions arising from experimental results. The questions can be divided into: 

1) are there any catalysts to promote anisotropic growth;
2) where does the growth of nanowires occur; and
3) how can the growth be achieved via either the supply of source material as a gas phase or through solid state diffusion?

The growth of nanowire can be obtained either by using any physical confinement to restrict the growth in one direction (template assisted growth) [17, 57, 80, 136, 137, 155, 266, 267] or preferential adsorption of source materials with the aid of a catalyst (VLS growth) [96, 97, 125]. For the growth of titania nanowires, the method of template assisted growth can be easily excluded because no porous membrane template was not used in this work. The role of a catalyst for the nanowire growth is to provide favorable sites and confinement of the growth in one direction as a liquid/solid phase. Usually, liquid droplets are formed by an eutectic alloy reaction between a source material (e.g., Zn for ZnO nanowire) and a metal catalyst (e.g., Au and Sn for Zn). This droplet with a certain solubility of the source material determined by the temperature acts as a preferential site for adsorbing source material from the gas phase. The adsorbed source material diffuses toward the interface between the liquid droplet and a substrate and then nucleate and grow as a 1-D nanostructure. A cap on the tip of a nanowire is commonly observed to be the characteristic feature resulting from the use of a catalyst because the liquid phase is solidified during the cooling process. Therefore, it is required to check the existence of a cap and chemical analysis of the cap by microscopy. No distinct cap were visible from SEM observation as discussed in chapter 3. Moreover, TEM analyses and EDS data for individual nanowire grown from pure Ti substrates at 600 °C for 8 hours
under an Ar gas atmosphere with the flow rate of 200 ml / min did not reveal any other elements except Ti and O as shown in Figure 3.8C. Therefore, it is concluded that the growth of titania nanowires for the growth of titania nanowires from pure Ti substrates is achieved not via the aid of a metal catalyst, but by other means.

The analysis of metal catalysts for β-Ti substrates is more complicated than that of pure Ti because of alloying elements such as Al, V, Cr and Fe in β-Ti alloy substrates. During the heat treatments, these alloying elements may segregate on the surface and form liquid phases if there are any eutectic phases between Ti and the alloying elements. By checking the phase diagrams of Ti with various alloying elements such as Al, V, Cr, and Fe, there are no binary eutectic reactions except for Fe. For Fe, there are two eutectic reactions [268].

\[
\begin{align*}
L &\leftrightarrow Fe_{lt} + TiFe_2 \quad (5.1) \\
L &\leftrightarrow Ti_{ht} + TiFe \quad (5.2)
\end{align*}
\]

where, Fe_{lt} and Ti_{ht} means low temperature stable Fe phase and high temperature stable Ti phase (β-phase), respectively. However, reactions (5.1) and (5.2) only occur at 1289 and 1085 °C, respectively. The temperature required for the eutectic reactions is much higher than the temperature of the growth of nanowires (700 °C). From the analysis of TEM-EDS on nanowires obtained from β-Ti substrates as shown in Figure 3.11D, an outer layer consisting of Ti, Al and O exists. Based on the ternary phase diagram of Ti, Al and O, the outer layer should be a solid phase rather than a liquid phase at the operation temperature (700 °C). Therefore, it is not possible to have any liquid phases between Ti and the alloying elements, which implies that the nanowire growth from the
heat treatment of β-Ti substrates is also not obtained via catalysts. In addition, the possibility of the formation of V$_2$O$_5$ should be checked because of its low melting temperature (~660 °C). However, the possibility to form V$_2$O$_5$ is very low considering the chemical concentration of V (5 wt %) and the free energy of formation of V$_2$O$_5$ (-20.12 kcal calculated at 700 °C). The most preferred oxide is Al$_2$O$_3$ from Ti alloys assuming the activity of each alloying elements is the same and calculating the free energy of formation of Al$_2$O$_3$, TiO$_2$ and V$_2$O$_5$. The least preferred oxide is V$_2$O$_5$ and the possibility of the formation is lowered in reality due to the lower concentration or lower activity of V in the alloys as discussed in chapter 2. Additionally, the formation of V$_2$O$_5$ has not been reported from the oxidation of Ti alloys unless the activity or the concentration of V is high enough to compensate for the difference in the formation energy of TiO$_2$ vs. V$_2$O$_5$.

Since the VLS mechanism is unlikely, one needs to consider other possibilities for the growth of nanowires either by vapor phase related growth or metal oxidation process via bulk diffusion. It is necessary to distinguish the vapor phase related growth (VS growth method) from metal oxidation processes which also require a gas containing oxygen. In the vapor phase related growth, it is required to have vaporized source materials for nanowires by thermal evaporation [116], laser ablation [115] and carbothermal evaporation [117, 118]. For the oxidation process, the metal from the substrate reacts with oxygen gas from the environment. In other words, there is no vaporized source material for the metal oxidation process. For the nanowire growth in the current method, it is necessary to investigate the possibility of having vaporized phases
containing Ti at the optimum temperature, 700 °C. There are two possibilities to generate vapor phases: i) \textit{direct vaporization of Ti} and ii) \textit{vaporization of oxide phases after the formation of an initial oxide layer}.

The vapor pressure of Ti at 973 K is 1.34×10^{-15} \text{ torr} \ [269]. Assuming that a Ti sample is heat treated at 700 °C for 8 hours and the surface area of the sample is 0.25×10^{-6} \text{ m}^2, the impinging rate of gas molecules on the surface can be calculated by using the following equation [270]

\[
v_{\text{max}} = \alpha \times 2.7 \times 10^{20} \frac{p[\text{bar}]}{\sqrt{MT}} \text{ [molecules m}^{-2}\text{s}^{-1}] \tag{5.3}
\]

where, \(\alpha\) is the accommodation coefficient of the gas molecules on the surface, which is usually unity, \(M\) is the molecular weight of the gas molecule and \(p\) is the pressure. The total number of impinging Ti gas molecules at 700 °C is 1.6×10^7 molecules. Assuming all the Ti gas molecules are converted to TiO\(_2\) by the following reaction

\[
\text{Ti (g) + O}_2\text{ (g)} \leftrightarrow \text{TiO}_2\text{ (g)} \tag{5.4}
\]

\[
\text{TiO}_2\text{ (g)} \rightarrow \text{TiO}_2\text{ (s)} \tag{5.5}
\]

and the number of moles of TiO\(_2\) (s) is 2.68×10^{-17}, the possible weight gain is estimated to be 2.1425×10^{-15} \text{ g}. This value is much less than the measured weight gain of a Ti sample heat treated at 600 °C for 8 hours, 0.037 mg. In addition, if there were vaporized Ti from pure Ti or Ti alloys during the heat treatment, there should be the deposition of Ti at the end of the tube (at a lower temperature) because condensation of vaporized Ti. No such condensation was observed.
For the calculation of the vapor pressure of Ti from Ti alloys, the vapor pressure of each element (ref) in the alloy will be defined by the following equation

$$P_i \; (\; Ti \; alloys\;) = P_0^i \gamma_i X_i \quad (5.6)$$

where, $\gamma_i$ is the activity coefficient of the $i^{th}$ element in the alloy and $X_i$ and $P_0^i$ are the mole fraction of $i^{th}$ element and the vapor pressure of $i^{th}$ element, respectively. Considering that $\gamma_i$ is less than unity, the vapor pressure of the $i^{th}$ element in the alloy system is less than the vapor pressure of pure element and subsequently the vapor pressure of Ti in the alloy samples is lower than that of the pure Ti sample. Therefore, it is unlikely that the nanowire growth from alloys is obtained by the vaporization of Ti.

There are some reports about the growth of nanowires with the aid of oxides which can easily produce the required vapor pressure for nanowire growth [271, 272]. For example, the growth of tungsten nanowires can be accomplished by the vapor phase of WO$_2$ formed initially [271]. In this experiment, tungsten metal was heated in an oxygen bearing environment at 1450 °C, which is higher than the tungsten oxide decomposition temperature. The vapor species, WO$_2$, condensed on a quartz substrate to form W nanowires [271]. The growth mechanism, as reported by Vaddiraju et al. [271], can be expressed by the following reaction with the associated Gibbs free energy.

$$WO_2(v) \rightarrow W (s) + O_2 \quad \Delta G = -267.33 \text{ kJ/mol K} \quad (5.7)$$

The vapor phase is generated due to a high temperature (1450 °C) and WO$_2$ condenses on preexisting tungsten oxide and subsequently decomposes to tungsten. They also reported the lack of a metal cap on the tip of nanowires grown at 700 °C for 10 minutes under an Ar gas atmosphere [271], which implies that the growth of nanowires is not achieved by
the VLS growth. Even though they did not provide a proper mechanism for the fiber growth, it can be deduced that the vapor phase of WO$_2$ and kinetics related with decomposition may have played roles in producing nanowires. The fact that the vaporization of oxides is sometimes much easier than that of metals leads to check the vapor pressure of the possible oxides of titanium.

It is possible to obtain titanium oxides such as TiO, Ti$_2$O$_3$ and TiO$_2$ as a result of oxidation of pure Ti and alloys. Based on literature, Groves et al. [273], the vapor pressure of each oxide can be calculated as shown below.

\begin{equation}
\log p_{\text{TiO}} = -\frac{29421}{T} - 0.583 \times 10^{-3}T + 10.43 \tag{5.9}
\end{equation}

\begin{equation}
\log p_{\text{TiO}_2} = -\frac{30361}{T} - 0.492 \times 10^{-3}T + 11.19 \tag{5.10}
\end{equation}

\begin{equation}
\log p_{\text{Ti}_2\text{O}_3} = -\frac{64700}{T} - 1.26 \times 10^{-3}T + 21.65 \tag{5.11}
\end{equation}

Based on these equations, the vapor pressures at 700 °C are $3.21 \times 10^{-18}$ torr, $2.44 \times 10^{-18}$ torr and $6.44 \times 10^{-44}$ torr for TiO, TiO$_2$, and Ti$_2$O$_3$, respectively. Because of low vapor pressures, it is obvious that the growth of nanowires is not vapor phase-assisted. In addition, the VSS growth in which a solid catalyst promote the growth of nanostructures by the diffusion of a source material from the gas phase through the solid catalyst as discussed in the chapter 2 is also eliminated because there are no vapor species of Ti even though the existence of catalysts is not completely ruled out.

The nanowire growth of metal oxides accomplished by thermal oxidation has previously been reported and there have been several concerns about the growth of nanowires. First, it is realized that there is a transition from a lateral oxide formation to
one directional growth based on the literature reports. The reason for the transition is not well understood and needs careful studies. Secondly, it is important to identify where the growth happens, which would give some clues about possible mechanism. From traditional oxidation theory, an oxide layer is formed by either the transport of cations or anions. If the formation of the oxide layer is obtained by the transport of cations such as metal interstitials, the oxide will grow at the surface by interactions between metal defects and chemisorbed oxygen. In contrast, the oxide growth occurs at the interface between the metal and the oxide by the diffusion of oxygen. Therefore, if the location of the growth of nanowires by metal oxidation process can be determined, it can at least be realized what kind of transport is responsible of producing the nanowires. In the following section, the location of the growth is determined experimentally. Consequently, a possible mechanism of the growth of nanowires by metal oxidation is proposed and justified with experimental evidences.

5.3 Experimental

The sample preparation followed the same procedure as discussed in the chapters 3 and 4 except an additional experiment using the lowest flow rate. For the lowest flow rate experiment at 700 °C for 8 hours, the outlet of the gas was closed by a clamp while still allowing an Ar gas flow through the orifice of the tube. The surface morphologies of specimens after the heat treatments were observed by SEM. For oxygen concentration variation experiment, first Ar having 500 ppm oxygen was introduced into the tube for 8 hours and then the gas was changed to an Ar gas having 5000 ppm oxygen for 4 hours
followed by cooling down to room temperature by turning off and opening the furnace while flowing Ar gas.

**5.4 Results and Discussion**

One important question that may aid in the understanding of the underlying mechanism is whether or not the nanostructure growth occurs at the tip of the nanowire or at the base. To get a preliminary idea, the following experiment was conducted. This experiment consisted of initiating nanowire growth under the optimal condition of 700 °C for 8 hours at the flow rate of 200 ml / minutes. After which, the processing temperature was increased to a higher temperature of 800 °C and held for 4 hours and then cooled down to room temperature. It was found that the nanowires maintained their structures even at the conditions which previously produced mostly faceted crystals or oxide layers as shown in Figure 5.1A. Not only did the nanowires maintained their structure they continued to grow. The growth after the temperature change produced a larger diameter fiber at the tip of the original nanowire produced under the optimal condition. The increase of the diameter of the nanowires is contributed to the reaction rate increase between Ti and oxygen at a higher temperature [261]. This result implies that the formation of nanowires actually occurs at the tip via the reaction between Ti and oxygen. If the growth of nanowires would be obtained by the diffusion of oxygen, the growth of nanowires would occur at the base of the nanowires. Therefore, it is not likely that the growth of nanowires is obtained by the diffusion of oxygen. Based on this result, it is
believed that Ti diffusion is only possible way to allow the growth of nanowires at the tip.

Naturally, a question arises regarding the transport of Ti. There are two possible transport paths for Ti by either surface diffusion or solid state bulk diffusion, which is the diffusion of Ti through the nanowires. The current hypothesis is that diffused Ti cations react with the chemisorbed oxygen from the gas phase causing the growth of the oxide nanowires at the tip. This is verified by extending the two-step heat treatment to include a third step where the temperature was reduced to 600 °C after the second step and the fiber was allowed to continue growing at the processing temperature. This produced the cattail nano-features as seen in Figure 5.1B. This reaffirms that the growth occurs at the tip.

Another step oxygen concentration experiment using two different oxygen concentrations such as 500 and 5000 ppm oxygen was performed in the same manner as step temperature experiments. Figure 5.2 shows the surface morphology when a β-Ti (5-5-5) sample was heat treated at 700 °C for 8 hours at the flow rate of 500 ml/min of the Ar gas having of 500 ppm and then the sample was kept in the Ar gas having of 5000 ppm for 4 hours at the same flow rate. As discussed in chapter 4, as the amount of oxygen in the gas phase increased, the growth of nanowires was inhibited. However, the growth of nanowires for step oxygen concentration experiment still continued as the amount of oxygen in the gas phase increased, which is consistent with the result of step temperature experiments. The results supports that the growth of nanowires continues even under the condition which does not allow the growth of nanowires when the density of nanowires is high. The length of nanowires increases from an average of 2 μm under 500 ppm of
oxygen to 4 \, \mu\text{m} after two step oxygen concentration experiment. It is realized that the morphology of nanowires is changed from wire to tapered wire as shown in Figure 5.2B, indicating that the transport of oxygen and the reaction between Ti and oxygen are faster at the tip, thus creating tapered morphology.

Various heat treatment duration time experiments were performed for 0.2, 0.5, 0.8, 1, 1.5, 3 and 6 hr at the flow rate of 500 ml/min of the Ar gas. For the duration time of 0.2 hr, the formation of cracked oxide scale is shown in Figure 5.3A. As the duration time was increased to 0.5 hr, the cracked oxide scale was connected to each other and there were white bumps on the top of planar oxide scale as seen in Figure 5.3B. Figure 5.3D shows separate islands after the heat treatment for 1 hr. These islands grew to longer nanowires as the heat treatment duration increased as shown in Figure 5.3E-G. It should be noted that \( r_l \), the lateral growth rate defined as the growth rate of radial direction of the nanowires did not change much as the heat treatment time increased. The initial diameter of the islands was about 30 nm. The diameter of the nanowires was maintained to be in the range of 30 \sim 60 \, \text{nm} based on TEM and SEM image analyses after the heat treatment at 700 \, ^\circ\text{C} for 8 hours. \( r_v \), the vertical growth rate, which is defined as the growth rate parallel to the length of the nanowires was estimated to be \sim 300 \, \text{nm/hr}. This result indicates that there is anisotropic reaction rate depending on the direction of the nanowires.

Based on these observations, the growth of nanowires by oxidation can be divided into four stages for the purpose of clarity. A schematic diagram of the growth stages is presented in Figure 5.4. In stage 1, an oxide layer is formed when a Ti or Ti alloy sample
is exposed to a gas containing a very low oxygen concentration at an elevated temperature. In stage 2, a transition from planar oxide scale to separate island formation occurs. These small islands are formed on top of the oxide layer. The diameter of the islands is approximately equal to that of nanowires. These separate island formation is explained by the transport of oxygen being rate limiting. If the transport of oxygen is rate limiting, the formation of separated islands is possible. The transport of oxygen in the region of islands is faster than that of the flat surface. Therefore, separate islands can maintain their morphology. These separate islands are formed and survived by morphological instability. This morphological instability is believed to be attributed to the transport of oxygen being rate limiting. If the rate limiting process is oxygen gas diffusion, the moving direction of the interface between metal and the oxide scale is opposite to the direction of oxygen transport, thus causing the morphological instability. However, if the rate limiting process is Ti diffusion, separate islands gradually disappear. Ti reaching the flat surface faster than the tip of the island as shown in Figure 5.5A causes the fast growth oxide scale in the region of the flat surface and the flat surface covers separate islands. It is also noted that the moving direction of the interface is the same as the direction of Ti diffusion, thus resulting in that there is no morphological instability, which is a key factor for the formation of separate islands.

In stage 3, separate islands grow into short nanowires. In order for short nanowires to survive and maintain their morphology, there should be anisotropic growth rate differences. What anisotropic growth rate difference means is that the growth rate on the tips is drastically faster than that of the sides, thus causing the growth of nanowires.
In the beginning of stage 3, the penetration of oxygen is possible to all the direction of a short nanowire as shown in Figure 5.3C. If there would be no anisotropic growth rate differences, the rough surface as shown in Figure 5.5B is formed. However, if there would be anisotropic growth rate differences, the growth of nanowires continues. It is concluded that the oxygen transport rate limit does not guarantee the growth of nanowires and the islands only evolve into nanowires when there is anisotropic growth rate differences. It is still not clear what the reason is for anisotropic growth rates. There are several possible ways to have anisotropic growth rates. There would be different reaction rates depending on the face of TiO$_2$ when it is exposed to oxygen gas. This reaction rate difference may be one of the reasons for anisotropic growth rate. In stage 4, as the density of nanowires increases, the permeability of oxygen is reduced and oxygen is only available at the tip of nanowires. Once Ti reaches the tip, the growth of nanowire continues without increasing the density of nanowires.

From temperature step experiments, it is concluded that the growth of nanowires is achieved by the diffusion of Ti and Ti is always available at the tip. In order to check this observation, the diffusion length of a Ti cation can be used. The chemical diffusivity ($\tilde{D}$) of Ti cation interstitials in a single crystal rutile TiO$_2$ in the temperature ranges of 900 – 1400 K was reported by Radecka et al. [274] and they presented the equation of the diffusivity in the following form:

$$\tilde{D} = (0.001 \pm 0.4) \exp\left(\frac{-48.7 \pm 8kJ/mol}{RT}\right) \text{cm}^2/\text{sec}$$

(5.12)
From equation (5.12), the diffusion length of titanium interstitials at 700 °C for 8 hrs is estimated to be 0.2 cm by using $\sqrt{Dt}$. This value is much larger than the length of the nanowires which is in the range of 2 – 5 μm. Consequently, it is possible to obtain the growth of the nanowires by the diffusion of Ti cations.

As discussed in the chapter 4, there is a relationship between the flow rate and the growth of nanowires for pure Ti samples on the morphology evolution of the surface while the relation of the growth morphology to the flow rate was not clear for Ti alloy samples. The effect of the flow rate can be explained by the equation (4.2). As the flow rate is increased, the thickness of the gaseous layer is decreased as defined in the equation. The reduced thickness causes faster transport of oxygen to the surface of the samples and faster transport actually increases the oxidation rate between Ti cations available at the surface and oxygen. The growth of nanowires is actually prevented by the growth rate increase because there is an increase of possibility in the coarsening of individual nuclei and it helps to form a continuous oxide layer instead of growth of individual nanowires.

In order to observe more clearer effect of oxygen transport, a possible lowest flow rate experiments were preformed. The thickness of the gas reaction boundary layer is actually the same as the physical dimension limit of the gas tube, which is roughly 1 inch because the thickness is inversely proportional to the flow rate. Therefore, the gas transport of oxygen is the most difficult in the case of the possible lowest flow rate. As shown in **Figure 5.6A**, the length of nanowires is in the range of 200 to 300 nm, which is shorter than those from β-Ti samples at the flow rate of 200 ml/min for the same period of the heat treatment. Nanowires were very straight and square shape. The diameter of
nanowires is in the range of 30 to 60 nm, which indicates that there is not much difference compared to the diameters of nanowires grown on Ti alloy samples at different flow rates. The fact that the length of nanowires is shorter than that of nanowires for the same duration on Ti alloys indicates that the transport of oxygen is actually responsible for the growth of nanowires. One question regarding the transport of oxygen puzzles us is that the diffusion coefficient of oxygen is around 0.203 cm$^2$/s at 70 °C [262], which implies that the transport of oxygen is not theoretically hindered at the processing temperature. Even though the reason for the difficulty of oxygen transport is not clear, it is suggested that the transport of oxygen is important for the growth of nanowires, evidenced by the possible lowest flow rate experiments. Plausible explanation for the growth of short nanowires is related with the oxygen concentration gradient. In the beginning, oxygen concentration gradient was very steep, but with time oxygen was used for the growth of the oxide layer and the replenishment of oxygen was not fast enough compared to other experiments using a higher flow rate such as 200, 500 and 1000 ml/min. Subsequently, the oxygen concentration gradient became low and even though the diffusivity of oxygen is fast, the flux of oxygen toward the surface may not have been large enough. Hence, the vertical growth rate was not that fast, thus resulting in shorter nanowires. A schematic diagram of oxygen concentration gradient for the experiment is represented in Figure 5.6B. It is suggested that the formation of nanowires may be partially related with the transport of oxygen gas. It was also observed that there was a difference in the growth rate of nanowires depending on the height of the surface as shown in Figure 5.6C. Longer nanowires were formed on higher locations of the surface.
and shorter nanowires were grown on lower locations of the surface. This fact also supports that the growth of nanowires is strongly related with the transport of oxygen. The ease of access of oxygen at the higher surfaces leads to longer fibers compared to the lower surfaces.

5.5 Conclusions

Nanowire growth on both pure Ti and alloy samples by simple heat treatments under the limited supply of oxygen was accomplished. From temperature step experiments, the growth of nanowires actually occurred at the tip of nanowires rather than the base of nanowires. No caps were observed from SEM and TEM analyses on the tips of individual nanowires from pure Ti and alloy samples. Thus, the possibility of the growth of nanowires by the aid of a catalyst was eliminated. Theoretical consideration of the possibility of binary eutectic reactions between Ti and alloying elements revealed that these reactions required higher temperatures than the processing temperature of 700 °C. The VS growth mechanism was also eliminated by considering theoretical calculation of the equilibrium vapor pressure of Ti containing species from both pure Ti and alloy samples. Based on the results from temperature step experiments and theoretical considerations, the diffusion of Ti was proposed to explain the growth of nanowires. The proposed mechanism consists of four stages. In stage 1, a cracked oxide or continuous planar oxide scale is formed. The transition from the planar oxide scale to separate islands occurs in stage 2 because of morphological instability caused by the oxygen transport being rate limiting. Once separate islands grow into short nanowires, there
should be anisotropic growth rate differences to maintain their morphology in stage 3. As the density of nanowires increases in stage 4, the penetration of oxygen molecules is not easy and oxygen molecules only interacts with Ti at the tip. The fact that the transport of oxygen is partially responsible for the growth of nanowires was experimentally supported by the lowest flow rate experiment and the observation of the growth rate difference depending on the surface.
Figure 5.1 SEM images of temperature step experiments at A: 700 °C for 8 hr followed by 800 °C for 4 hr; and B: 700 °C for 8 hr followed by 800 °C for 2 hr and 600 °C for 2 hr.
Figure 5.2 The surface images after step oxygen concentration experiments at 700 °C A: at a low magnification and B: a high magnification showing tapered nanowires.
Figure 5.3 Scanning electron micrographs of β-Ti samples with various durations of the heat treatment at 700 °C after A: 0.2, B: 0.5, C: 0.8, D: 1, E: 1.5, F: 3 and G: 6 hr, respectively.
Figure 5.3: Continued
Figure 5.3: Continued

Continued
Figure 5.3: Continued
Figure 5.4 A schematic diagram of each stage of the growth of nanowires
Figure 5.5 A: A schematic diagram of the surface evolution for both the rate limiting step of Ti and oxygen and B: a schematic diagram for the surface evolution with both no anisotropic growth and anisotropic growth rates.
Figure 5.6 A: Scanning electron micrograph of β-Ti samples for the zero flow rate after the heat treatment at 700 °C for 8 hours B: a schematic diagram of PO$_2$ concentration plots for two time periods C: scanning electron micrograph of β-Ti samples for the flow rate, 500 ml/min after the heat treatment at 700 °C for 3 hours.
Figure 5.6: Continued
CHAPTER 6

EXTENSION OF THE METHOD TO THIN FILM AND APPLICATIONS WITH PRELIMINARY RESULTS

6.1 Introduction

Ti thin film has been widely used in electronic device fabrications as adhesion layers and electrodes [275, 276]. If the growth of nanowires on Ti thin film happens by our simple method, it can be used to fabricate nanowire gas sensors [47, 169, 184], FET devices [19, 30], and photonic devices [267, 277]. It also decreases the dimension of such devices, thus reducing power consumption. It also gives advantages to be incorporated into current electronic device fabrication processes, thus increasing applications of the nanostructures in real devices. Therefore, the growth of nanowires on Ti thin film was explored and the results are discussed.

Ti and Ti64 have been widely used for biomedical applications as hip joint replacements and dental implants because of their mechanical and chemical stabilities [278]. However, it is believed that the bioactivity which is defined to promote adhesion and growth of cells on Ti and Ti64 is poor [278]. Therefore, surface modifications have
been performed to enhance the bioactivity by increasing the surface area [197]. There have been reports of direct depositions of coatings such as TiO$_2$ and HA (hydroxyapatite) on Ti or Ti64 plates to improve the bioactivity [197]. There are problems to use HA coatings because it has poor adhesion to the metal and their mechanical stability is weak [279, 280]. Therefore, TiO$_2$ coating by thermal spray methods has been widely used [281]. Because enhanced surface areas can be very beneficial to improve the bioactivity [221, 282], it is desirable to modify the surface of thermal spray coated TiO$_2$ with the growth of nanowires. In this section, the growth of nanowires on TiO$_2$ coating is discussed and results of preliminary biomedical tests are reported.

6.2 Experimental

6.2.1 Ti thin film deposition

Titanium thin films were prepared by using a d.c. magnetron sputtering system (Denton Discovery 18, Denton Vacuum, NJ). The target was a titanium disk (purity 99.6%, Alfa Aesar) of 3 inch diameter and the target to substrate distance was 13 cm and d.c. power of 120 W was used. Before each sputtering experiment, the chamber was pumped down to $1 \times 10^{-7}$ torr and the target was pre-sputtered in a pure argon atmosphere for 5 minutes to remove the surface oxide layer of the target. Polished alumina substrates (MTI Corp, Richmond, CA) were used for thin film deposition. Argon was introduced into the main chamber to obtain Ti film and the flow rate of Ar was 43 sccm. At the given flow rate, the operational pressure remained at 5 mtorr. The temperature of the main chamber was heated to 400 °C. When the temperature of the chamber reached 400 °C, the deposition of Ti metal thin film started and the deposition time was 20 minutes. After Ti
metal film deposition, thin Au metal layer was deposited using a CrC 150 desktop sputtering system for 20 seconds to check the effect of the growth by Au catalyst. The Ar gas at the flow rate of 1000 ml/min was introduced into the tube. The tube was held at 800 °C for 30 minutes with a heating rate of 30 °C/min to reach the temperature.

### 6.2.2 TiO₂ coating on Ti64 samples by thermal spray coating

TiO₂ coated Ti64 samples were obtained from Dr. Lima at National Research Council of Canada and the coating process is described as follows. TiO₂ coatings were fabricated by a high velocity oxy-fuel (HVOF) technique on a Ti64 substrate. The powder for the TiO₂ coatings had a particle size distribution from 5 to 20 μm and was obtained from Altair Nanomaterials Inc. The metal substrates were grit-blasted to roughen the surface before spraying for the purpose of increasing adhesion between the TiO₂ coating and the Ti64 substrate. The powder was thermally sprayed for 2 minutes on the metal substrates via a HVOF technique using an oxy-propylene based torch. The black gray color coatings were obtained on the substrates. The thickness of the coatings was approximately 100 μm. The coating was characterized by XRD and its crystal phase was identified as a mixture of rutile and anatase, but its dominant phase was rutile. More detailed information about the coatings and coated film characterization can be found elsewhere [281].

### 6.2.3 Characterization

The surface morphologies of Ti thin films and TiO₂ coated Ti64 samples after heat treatments were observed by a high resolution field emission scanning electron
microscope (FE-SEM, Model Sirion, FEI). The samples were coated with Au thin film before SEM observations to prohibit electron charging effect.

For nanowires grown on TiO$_2$ coated Ti64 sample after heat treatments, nanowires were collected by the same manner and were sent to Dr. Cai at Georgia Institute of Technology for characterizations by a HRTEM (Model 4000EX, JEOL) at an operation voltage of 400 kV.

**6.2.4 Experimental method for biomedical tests**

The cell culturing experiments were performed by Daniel Perez of Biomedical Engineering at Ohio State University. The experimental procedures are described as follows. At first, a polished Ti64, oxidized Ti64 and nanowires grown on a Ti64 sample were prepared, sterilized and human osteosarcoma (HOS) cells (ATCC, USA) were seeded on top of the substrates at a density of $5 \times 10^4$ cells/cm$^2$. The tests of the cell culturing were performed for 15 hours, and 10, 25, and 35 days. Alkaline phosphatase (ALP) activity, an early marker of bone differentiation, was measured to monitor light absorbance. ALP activity was then calculated from the slope of the absorbance versus time curve.

**6.2.5 Procedure for sensing test**

Sensing tests were performed by attaching Au electrodes on top of TiO$_2$ nanowires grown on Au-catalized Ti thin film deposited on alumina substrates by d.c. sputtering. The sensor was held in a tube furnace and heated to 500 °C in 10% oxygen atmosphere and then CO gas was introduced into the furnace. The sensor response was
tested in the range of 250 to 1000 ppm CO and the change of the resistance was measured at each CO concentration.

6.3 Results and Discussion

6.3.1 The growth of nanowires on Ti thin film with and without Au catalyst

Ti thin films deposited on alumina substrates were used to check the possibility of the formation of nanowires. The surface morphology of Ti film before the heat treatment is shown in Figure 6.1A. Fine crystals less than 100 nm in size were formed on an alumina substrate. The thickness of Ti thin film was estimated to be 200 nm. Figure 6.1B shows the surface morphology changes of Ti thin film without Au catalyst after a heat treatment at 800 °C for 30 min at the Ar gas flow rate of 1000 ml/min. There were no nanowires and well faceted crystals less than 1 μm in size were connected to each other to form continuous oxide layer. The thickness of Ti thin film was only 200 nm and most of the film was easily oxidized after the short duration of oxidation. Au thin film on Ti bulk could accelerate the diffusion of Ti to the surface without proposing a plausible mechanism [277]. In order to grow TiO₂ nanowires from Ti thin film, Ti diffusion to the surface through the oxide should be fast to overcome the diffusion of oxygen. Au thin film was deposited on Ti thin film at room temperature for 20 sec and the thickness of Au thin film was estimated to be less than 10 nm by considering the power of the sputtering system and the sputtering yield rate of Au. The prepared sample was heat treated under the same condition as the previous one. Figure 6.1C shows the growth of nanowires and the length of nanowires ranging from 0.1 to 1 μm. Caps on the tips of nanowires were
observed. This observation is different than that of Lee et al. [79] who reported the growth of titania nanowires with Au catalyst but did not observe Au caps. Figure 6.1D shows the morphology of Ti bulk which had Au catalyst thin film before the heat treatment under the same condition. No nanowires were observed and the surface morphology was similar to that of Ti film without Au catalyst after the heat treatment. The reason for no nanowire formation is believed to be that bulk Ti has plenty of Ti supply compared to Ti thin film and there may be coarsening of TiO₂ nanowires due to abundant supply of diffused Ti. Nanowires with caps were observed from Ti64 bulk with Au catalyst after the same heat treatment as shown in Figure 6.1E.

At this time, the difference between Ti and Ti64 bulk with Au catalyst is not fully understood. There are no eutectic alloys between Au and Ti to reduce the reaction temperature as discussed in chapter 3. The melting temperature of Au can be decreased to 600 ~ 700 °C when the particle of Au is comparable to 3 ~ 5nm [233, 283]. If Au thin film was not continuous and consisted of small particles less than 5 nm, the melting of Au occurred and liquid droplets acted as a catalyst. However, there is also the possibility of the growth by the VSS (Vapor-Solid-Solid) mechanism. In the future, the cap needs to be investigated under a TEM to check the chemical composition along with in-situ experiments. By these experiments, the role of Au catalyst would be revealed.

6.3.2 Heat treatment of TiO₂ coated Ti64 samples

As deposited TiO₂ coating on Ti64 samples showed dark gray color which indicated that TiO₂ was reduced and there were plenty of Ti interstitials. Figure 6.2A shows the surface image of TiO₂ coating before the heat treatment showing characteristic
microstructure of thermal spray coatings. Because of the high velocity of partially molten TiO\textsubscript{2} powders, the surface morphology of the coatings show rough and connected platelets. It was noticed that nanowires were not inherent structure of TiO\textsubscript{2} by thermal spray coating but the consequent product of gas heat treatments.

Figure 6.2B shows wire like products observed on TiO\textsubscript{2} coated Ti64 substrates after a heat treatment in Ar at 700 °C for 8 hours at the flow rate of 1000 ml/min. Most of the nanostructures observed were nanowires and some of them were nanobelts and nanowhiskers. Nanowires formed looks like a stack of polyhedrons which are similar to an equilibrium shape of TiO\textsubscript{2} rutile. Other nanostructures were nanobar showing ripple on the sides as shown in Figure 6.2D. The nanowires formed have irregular distributions and lengths in the range of 2 μm to 6 μm. The diameters of the long acicular nanowires are less than 500 nm.

The phase of nanowires could be determined by XRD. However, because of the thickness of TiO\textsubscript{2} coating (100 μm), the XRD also collects the phase information of the TiO\textsubscript{2} bulk and it is not suitable for the phase characterization. Therefore, the phase of nanowires was analyzed by HRTEM. Figure 6.3A shows a TEM image of individual nanowire. The length and diameter of the nanowire was approximately 6 and 0.3 μm, respectively. The image of the tip at a high magnification is shown in Figure 6.3B and there was no cap that existed on the tip, indicating that the growth of nanowires was not by the VLS mechanism. In the inset, the SAED pattern of the tip resulting in rutile phase of TiO\textsubscript{2} with the zone axis of [-112] is given. The growth direction was obtained from the
lattice image presented in Figure 6.3C and the direction of the growth was determined to be [110].

A TEM image of another nanowire is presented in Figure 6.4A. The length and diameter of the nanowire were approximately 5.2 and 0.25 μm, respectively. The SAED pattern is shown in Figure 6.4B and the phase was determined to be rutile. The zone axis was [0-20]. Through the lattice image of the location marked as “2” in Figure 6.4C, the growth orientation was determined to be <100> by matching an interplanar spacing value, 0.229 nm. These multiple growth orientations may be caused by polycrystalline TiO$_2$ nanoseeds used in the thermal spray coating, if the growth of nanowires mimic the orientation of the base or nanoseeds.

Figure 6.5 shows the surface morphology changes by changing the Ar gas flow rate. Well developed nanowires were formed by a heat treatment at 700 °C for 8 hours at the flow rate of 500 ml/min. The length of nanowires was in the range of 2 to 3 μm in Figure 6.5A. It seemed that the length of nanowires was shorter than that of nanowires grown at the flow rate of 1000 ml/min. As the flow rate increased to 1500 ml/min, well faceted crystals were formed and no nanowires were observed as shown in Figure 6.5B.

Yoo [186] reported the formation of nanowhiskers after reoxidation of nanofibers formed on TiO$_2$ template at 700 °C. It was argued that the growth of nanowhiskers was caused by Ti$^{3+}$ interstitials which was generated during his nanocarving process. Even though there have been no reports about extensive growth of nanowhiskers by reoxidation process, there were a few reports about reoxidation at the surface scale [284, 285]. It was proposed by Onishi et al. [286, 287] that Ti$^{4+}$ interstitial diffusion to the
surface occurred during the reoxidation of reduced TiO$_2$. The growth of TiO$_2$ by the reaction of O$_2$ with mobile Ti$^{3+}$ from the reoxidation process was also reported by Smith et al. [288]. Henderson et al. [289] proposed that excessive Ti produced from the reduction of TiO$_2$ sinks in the bulk of TiO$_2$. Generation or extinction of Ti$^{3+}$ ions during reoxidation or reduction processes are repeated between the bulk and the surface.

The reduced TiO$_2$ coating on Ti64 samples was converted to stoichiometric TiO$_2$ by annealing samples under a stagnant air atmosphere at 700 °C for 4 hours. After the annealing, the color of the coating changed from dark gray to white, which implied that the annealed coating was stoichiometric. The surface image of TiO$_2$ after the annealing is presented in Figure 6.6A. The surface morphology of TiO$_2$ coated Ti64 shows similar structures compared to the surface image of samples without annealing as shown in Figure 6.2A. The surface morphology changes of annealed TiO$_2$ coating after heat treatments at 700 °C for 8 hours at the Ar flow rate of 1000 ml/min are shown in Figure 6.6B. No nanowires were observed. The reason for the disappearance of nanowires can be explained by considering that Ti interstitials were consumed during the air annealing and slow supply of Ti interstitials therefore hindered the growth of nanowires during heat treatments.

### 6.3.3 Sensing test of nanowires grown on Ti thin films

Figure 6.7 shows the sensitivity (R$_0$/R) of the sensor with TiO$_2$ nanowires at 500 °C. The CO sensitivity, R$_0$/R, is defined as the relative resistance, where R$_0$ is the resistance of the sensor in 10% O$_2$ background gas. At 500 °C, the baseline of the sensor is stable and the response time is less than 1 minute. Compared to the sensing behavior of
TiO$_2$ thin film sensor, the sensor with TiO$_2$ nanowires shows better sensitivity. The sensitivity of semiconducting metal oxides has been further enhanced by the incorporation of catalytic noble metals on the surface of the base metal oxide sensor [290].

6.3.4 Cell culturing test

Figure 6.8A shows increased cell proliferation on TiO$_2$ nanowires, with respect to flat Ti64 and TiO$_2$. The functionality of bone cell has been recognized by ALP activity. ALP activity on TiO$_2$ nanowires, with respect to flat Ti64 and TiO$_2$ substrates after 15 hours and 10 days of culture (p = 0.019 and 0.042, respectively) is increased as shown in Figure 6.8B. ALP activity on flat Ti64 and TiO$_2$ remained relatively constant at any given time.

6.4 Conclusion

The growth of TiO$_2$ nanowires on Ti thin films was only achieved with Au catalyst. While there was no growth of nanowires on Ti bulk samples with Au catalyst, the growth of nanowires on Ti64 samples with Au catalyst was observed. Caps on the tips on nanowires on both Ti thin films and Ti64 bulk samples were present, indicating that the growth of nanowires on them was achieved by the aid of Au catalyst.

The growth of nanowires on reduced TiO$_2$ coated on Ti64 samples was observed. However, once reduced TiO$_2$ coating was fully recovered to the stoichiometry of TiO$_2$ after annealing in air, the growth of nanowires was not achieved, thus indicating that the
growth of nanowires was related with the diffusion of Ti cations. It was also realized that the growth directions of nanowires can vary; [110] and [100] were identified in this study.

Preliminary biomedical tests showed that the gas sensitivity and ALP activity were improved when TiO$_2$ nanowires existed on the samples compared to other controlled samples.
Figure 6.1 A: the surface image of Ti thin film, B: the surface image after the heat treatment at 800 °C with 1000 ml/min for 0.5 hour with Au catalyst, C: the surface image after the heat treatment at the same condition without Au catalyst, D: the surface image after the heat treatment at the same condition with Au catalyst on Ti bulk and E: the surface image after the heat treatment at the same condition with Au catalyst on Ti64 bulk.
Figure 6.1: Continued
Figure 6.1: Continued
Figure 6.2 A: the surface image of TiO₂ coating on Ti64 before, and B: after the heat treatment at the flow rate of 1000 ml/min at 700 °C for 8 hours, C: an image showing a nanowire consisted of polyhedrons and D: an image showing a nanobar and nanobar having ripple on the sides.
Figure 6.2: Continued
Figure 6.3 A: A TEM image showing individual nanowire, B: an image showing the tip of the nanowire and the inset showing the SAED pattern of the nanowire and C: the lattice image of the nanowire.
Figure 6.3: Continued
Figure 6.4 A: A TEM image showing individual nanowire, B: the SAED pattern of the nanowire and C: the lattice image of the nanowire.

Continued
Figure 6.4: Continued
Figure 6.5 A: the surface image of TiO$_2$ coating on Ti64 samples after the heat treatment at 700 °C for the flow rate of 500 ml/min for 8 hours and B: at the same conditions except the flow rate of 1500 ml/min.
Figure 6.6 A: the surface image of TiO$_2$ coating after air annealing at 700 °C under an air atmosphere and B: the surface image after the heat treatment at 700 °C at the flow rate of 1000 ml/min for 8 hours.
Figure 6.7 Sensitivity change of the sensor with TiO$_2$ nanowires for CO concentration from 250 to 1000 ppm at 500 °C.
Figure 6.8 A: Osteoblast-like cell proliferation (‘*’ indicates statistically significant difference) and B: ALP activity of osteoblast-like cells grown on Ti-based substrates (‘***’ indicates statistically significant difference) (Courtesy to Daniel at The Ohio State University of Biomedical Engineering).
CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

7.1 Conclusions

Instead of using expensive and complex methods to produce 1D structures, a simple direct oxidation method has been developed to produce either pure TiO$_2$ nanowire or nanowires covered by Al rich outer layer under a limited supply of oxygen. The dimension of the nanofibers ranged from 30 to 60 nm in diameter and their length were between 500 nm to several $\mu$m depending on Ti alloy samples. Experimental parameters such as flow rate, heat treatment temperature, and gas constituent have effects on the morphology of the surface on the samples. Based on various conditions, pure TiO$_2$ nanowires were only grown on pure Ti samples at the heat treatment temperature, 600 °C with an Ar flow rate, 200 ml / min. As the heat treatment temperature increases, well faceted crystals were formed and connected to each other to form continuous oxide scale.
As the flow rate increases, the formation of nanowires were hindered and oxide layer were formed rather than the growth of nanowires. With the effect of the heat treatment temperature, separated crystals were formed at a low flow rate but separated crystals were connected as the flow rate increases. The phase of nanowires is determined to be rutile based on the SAED pattern from TEM analyses.

For Ti alloy samples, the growth of nanowires was accelerated in terms of the density and length of nanowires. The effects of the heat treatment on the surface morphology were similar to those of pure Ti samples. However, the effect of the flow rate was not eminent as those of pure Ti samples. Consequently, the growth processing window for Ti alloys is larger than that of pure Ti samples with respect to the flow rate. The phase characterization of nanowires by XRD, TEM and EDS analyses indicated that the inner rutile core was covered by Al rich outer layer.

At this point, the growth mechanism for nanowire formation is not well established but the growth of nanowires is at least partially related with the transport of oxygen from the gaseous layer. Based on experimental observations, a feasible mechanism is proposed.

7.2 Recommendations for future work

It is commonly believed that the properties of nanomaterials in any form of 1-D structure can be dramatically different from those of bulk counterparts because of their enhanced surface areas, different electronic structures, and quantum confinement effects. It is very useful to measure the field emission, photocatalytic, photoelectronic, and
electronic properties of the nanowires at the macroscopic scale as the sum contribution from each nanowire to confirm the unique and interesting properties. After observing the macroscopic properties, it is worthwhile to measuring the properties of an individual nanowire. While the properties of pure individual TiO₂ nanowires have been reported, there is no report on the properties of a heterogeneous nanowire which has a core shell of TiO₂ covered by an outer layer. Therefore, it is very useful to measure the properties of an individual heterogeneous nanowire at the nanoscale. In addition, the controllability of the morphology of nanowires from this technique can be advantageous. For example, the sharper tip may be used in field emission applications where a fine point is required. By changing oxygen concentration during the heat treatment, a sharper tapered tip can be obtained and the field emission properties can be measured on these nanowires.

In the previous chapters, the growth of nanowires on Ti and Ti alloys by direct oxidation under limited supply of oxygen has been discussed. From TEM and EDS analyses of Ti alloys, it was found that an outer Al rich sheath or layer covered an inner shell of TiO₂ oxide after heat treatments under a limited supply of oxygen. However, even though it was found that the use of alloys containing the Al element is not necessary to produce nanowires, it is obvious from the results discussed previously that the density and growth of nanowires were promoted under the presence of the Al element. Therefore, it is important to understand the role of Al in causing these effects and there are several questions regarding the role of Al. First, the reason why the outer layer forms is not still clear nor is it clear if the outer layer formed at the same time as the TiO₂ inner shell. Second, the role of the outer layer in the growth of the nanowire is not yet understood.
Etching of the outer layer can be used to identify if the outer layer is the consequence of the use of Ti alloy substrates. NaOH is a common etchant to remove alumina, aluminum, and TiO$_2$. If the outer layer is carefully removed by the etchant at an initial stage of nanowires growth and heat treated again, the role of the outer layer may be revealed. Additionally, even though the formation of Al$_2$TiO$_5$ is highly unfavorable by thermodynamic consideration, there may be an unknown Al-Ti-O compound which may act as a liquid catalyst at the heat treatment temperatures. The mechanism would be much clearer if the formation of any liquid phase would be indentified by in-situ SEM observations.

The other interesting fact is the observation of possible orientation relationships between highly textured $\beta$-Ti alloy and nanowires. These well aligned nanowire structures can be advantageous for specific applications such as dye-sensitizer solar cells or field emission devices. If the epitaxial relationship could be identified, it would be very useful to extend the possibility of these well ordered nanowires in the application field and build up fundamental insight of the growth mechanism. To date, other metals such as V, and Ta were not successful platforms for producing nanowires. Other metals such as Zr and TiAl could be tested to gleam general understanding of the formation of nanowires.

Using the bulk Ti alloys to produce nanowires is sometimes advantageous but pure Ti and Ti alloy thin films are required to grow nanowires for small electronic devices. From the result of preliminary experiments using Ti thin film with Au thin film as a catalyst, the formation of nanowires on the thin film is easily obtained. In addition,
Ti alloy thin film can be easily produced by preparing Ti alloy target. After depositing Ti alloy thin films, heat treatment tests can be performed to check for the possibility of nanowire growth on the alloyed thin films. For the Ti thin films with Au catalyst, the role of Au is still not clear because there are no Au-Ti eutectic alloys which form a liquid phase at heat treatment temperatures (700 and 800 °C). Therefore, the mechanism of the nanowire growth from Ti thin film with Au is not VLS (Vapor-Liquid-Solid) but VSS (Vapor-Solid-Solid). Currently, there is no clear understanding about the formation of Au islands. The oxygen solubility of Au is very low and almost zero. The diffusion of oxygen on Au islands would be achieved by the surface diffusion rather than solid state diffusion because of the negligible oxygen solubility. If the Au catalyst is replaced with Ag, which has higher oxygen solubility than Au, the growth of nanowires is expected to be accelerated because the diffusion of oxygen is achieved by not only the surface diffusion but also the bulk diffusion. Therefore by conducting these experiments, the mechanism for the growth of nanowires on the thin film could be clearly established.

It can be advantageous to control the location of the growth of nanowires for specific applications such as biomedical coating. From the previous results, the selective growth of nanowires at specific locations of a substrate was already confirmed by either positioning small β-Ti grains around the grain boundary of α-Ti grains or using rough surface of the substrate. For patterned or selective growth of nanowires on substrates, the difference of the growth rate of nanowires on places having various heights on the surface can be used. When nanowires grew on a place at a higher surface than the majority of the surface, longer nanowires were formed. By using different growth rates...
depending on the height, it is possible to accomplish a patterned growth on a substrate. Patterned trenches can be prepared with the use of lithography techniques. Patterning the nanowire growth by the use of trenches or other features may lead to an expansion of the application fields for these materials.
BIBLIOGRAPHY


