VISIBLE LIGHT ABSORPTION BY NITROGEN-DOPED TITANIUM DIOXIDE THIN FILMS WITH \{001\} FACETS FOR PHOTOCATALYSIS

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Masters of Science

In
Chemistry: Materials Chemistry

By
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I certify that I have read *Visible Light Absorption by Nitrogen-Doped Titanium Dioxide Thin Films with {001} facets for Photocatalysis* by Mana Moarrefzadeh, and this work meets the criteria for approving a thesis submitted in partial fulfillment of the requirement for the degree Masters of Science in Chemistry: Materials Chemistry at San Francisco State University.

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Titanium dioxide is a nontoxic, inexpensive, and highly efficient photocatalyst that has been extensively studied for degradation of organic pollutants in water. However, because of the wide band gap energy of titanium dioxide, only a small UV fraction of solar light (3-5%) can be utilized. Therefore, it is of great interest to find ways to extend the absorption wavelength range of titanium dioxide to the visible region without decreasing the photocatalytic activity. Theory suggests that anion doping of titanium dioxide has considerable effects on the band gap alteration.\textsuperscript{1,2} Significant progress was made in this area by Liu and co-workers\textsuperscript{3}, who reported the synthesis of visible light responsive nitrogen doped micro-sized anatase titanium dioxide powders. In this study, in order to utilize visible light in photocatalytic reactions, nitrogen-doped titanium dioxide films were prepared hydrothermally using different methods: (a) TiN method; TiF\textsubscript{4} and TiN as the titanium and nitrogen source and sapphire as substrate (secondary and primary growths), (b) NaN\textsubscript{3} method; TiF\textsubscript{4} and NaN\textsubscript{3} as the titanium and nitrogen source and sapphire as substrate (secondary and primary growths, also RHS: rapid hydrothermal synthesis). The resulting anatase films are polycrystalline, continuous, and evenly coat the substrate to a thickness of approximately 700 nm. Our study shows that N,F co-doped titanium dioxide films narrow the band gap of titania and show a significant shift of the absorption edge to a lower energy in the visible region, 580-800 nm. Therefore, nitrogen doping has important effects on the photocatalytic activity using visible light.
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1. Introduction

Titanium dioxide (TiO$_2$) has received attention as a promising material for photochemical applications because of its photocatalytic activity, long-term stability, and nontoxicity. However, the large band-gap of TiO$_2$, and low quantum efficiency restrict its widespread adoption as a commercial photocatalyst. The band-gap of TiO$_2$ is 3.2 eV and therefore it becomes active only under ultraviolet (UV) light. Thus, only a small fraction of the solar spectrum that reaches earth's surface (~5%) can be utilized. To overcome this problem, this thesis focuses on creating visible light absorbing TiO$_2$, which is accomplished by doping the metal oxide with nitrogen during synthesis. Many groups have demonstrated the substitution of nitrogen as a nonmetal atom for oxygen in the anatase lattice. Asahi et al. showed that N-doping shifted the absorption edge of anatase to a lower energy, thereby increasing the photoreactivity in the visible-light region. Although N-doped TiO$_2$ has been widely fabricated and studied for photocatalysis under visible light irradiation, most of the published research examined powders. In this thesis, a new N,F co-doping method is introduced that promises a more cost/time effective method for the preparation of anatase thin films that not only absorb visible light because of a lowered band-gap (N-doping) but also show photocatalytic activity due to a surface dominated by {001} facets (F-doping), which are very effective for photocatalytic oxidation chemistry. These visible light absorbing films may be suitable for energy and environmental remediation applications.

1.1. Titanium dioxide

Titanium dioxide, also known as titanium (IV) oxide or titania, is the naturally occurring oxide of titanium, chemical formula TiO$_2$. When used as a pigment, it is called titanium white. It appears as a white solid, is insoluble in water, and odorless. The three minerals phases of TiO$_2$ are rutile, anatase and brookite and the unit cell of each phase is
shown in Figure 1. Rutile and anatase have a tetragonal lattice belonging to space groups P4_2/mnm (a=b=4.5922 Å, c=2.9574 Å) and I4_1/amd (a=b=3.7845 Å, c=9.5143 Å), respectively. Brookite has an orthorhombic lattice with space group P_{baa} (a=9.174 Å, c=5.449 Å, 5.138 Å). Rutile is the most abundant of these three phases and is the thermodynamically most stable phase of TiO_2. The metastable anatase and brookite phases convert irreversibly to the equilibrium rutile phase upon heating in air at 600°-800°C.

Figure 1. Unit cell for rutile (left), brookite (center), and anatase (right). Red and magenta spheres represent oxygen and titanium atoms respectively. Individual unit cells are not drawn to scale. From reference 6.

1.2. Applications of titanium dioxide

TiO_2 is the most widely used white pigment because of its brightness and very high refractive index. Overall, about 80% of the world's TiO_2 consumption is for paints and varnishes as well as paper and plastics. Other pigment applications such as printing inks, fibers, rubber, cosmetic products and foodstuffs account for another 8%. The balance of TiO_2 consumption is used in other applications, for instance the production of
titanium metal and alloys, glass and glass ceramics, electrical ceramics, catalysts, electric conductors and chemical intermediates. These applications to a large extent depend on its physical and chemical nature, which are related to its crystal structure, grain (crystal) size, morphology, and even surface structure. For example, TiO$_2$ in powder form is an effective opacifier, where it is employed as a pigment to provide whiteness and opacity to products such as paints, coatings, plastics, papers, inks, foods, medicines as well as most toothpastes. When deposited as a thin film, its refractive index and transparency make it an excellent reflective optical coating for dielectric mirrors and some gemstones like "mystic fire topaz". Additionally, TiO$_2$ films have potential uses for a number of electronic device applications such as dye-sensitized solar cells (DSSC) as well as antireflective coatings, gas sensors, electro-chromic displays, and planar waveguides. The high dielectric constant of TiO$_2$ allows its consideration as an alternative to silicon dioxide for ultrathin gate oxide dielectrics used in memory and logic devices.

Anatase TiO$_2$ is a potential low-cost water remediation photocatalyst to remove contaminants from water particularly in developing nations where access to clean drinking water remains a persistent problem. Many of the current water remediation techniques are either too costly or result in the additional generation of waste that needs to be treated further. Common remediation techniques include activated adsorbent materials and chemical treatment. The use of absorbent materials such as activated carbon or iron oxides allows for collection of pollutants on their surfaces from water. Nevertheless, the spent adsorbent then becomes a contaminant to be disposed of. Chemical treatment to remediate organic toxins include the use of chlorine, chloramine, or ozone and can result in potentially carcinogenic byproducts. TiO$_2$ is an effective photocatalyst and may be part of the solution for point-of-use applications to remediate water borne pollutants and microbes, and thus provide drinking water in remote areas.

A photocatalyst is a material that is activated by light and then modifies the rate of reaction without undergoing chemical transformation itself. In this respect, a transition
metal semiconductor such as TiO$_2$ is ideal. TiO$_2$ is chemically and thermally stable under a wide range of conditions and environments. It is also abundant and therefore inexpensive to prepare. If TiO$_2$ can be modified by chemical doping to absorb visible light and remain highly reactive in its photoactivated state, then this would significantly advance the field of photocatalysis. Of the three phases, anatase is the most active photocatalytic material and because of this property and many other potential applications, it is one of most heavily studied metal oxide semiconductors. Anatase in nanoparticle form is the basis of electron transfer in DSSC. A dye molecule is adsorbed to the TiO$_2$ surface and absorbs light injecting an e$^-$ into TiO$_2$. In addition, TiO$_2$ thin films perform critical functions as an electron transport layer (ETL) and also as a hole-blocking layer in perovskite based solar cells.

1.3. Photocatalytic activity of titanium dioxide

The photocatalytic properties of titanium dioxide were first discovered by Akira Fujishima in 1967 and published in 1972. It was discovered that a rutile TiO$_2$ (001) singlecrystal splits H$_2$O to H$_2$ and O$_2$ under photoelectrochemical conditions (< 415 nm; 3.0 eV the band gap of rutile). The rutile in this photochemical reaction functioned as the anode producing O$_2$(g) while H$_2$(g) was generated at the cathode, platinum black. TiO$_2$ has potential for use in energy production because it is an effective photocatalyst for H$_2$ production under ultraviolet (UV) light particularly in the anatase form. In H$_2$ evolution experiments, H$_2$ production is assisted by a small amount of platinum nanoparticles, which are deposited on the TiO$_2$ surface. Under UV irradiation, electrons and holes are produced. The electrons migrate to the platinum due to the formation of a depletion layer while hole states migrate to the oxide surface. The strong oxidative potential of the positive holes oxidizes water (or other electron donor such as methanol or virtually any organic compound) to create protons and hydroxyl radicals. It is this
strong oxidizing power of hole surface states that allows TiO$_2$-mediated photocatalysis to be very effective in the photodisinfection of microbes, inactivation of cancer cells, odor control, and as well as photocatalytic water splitting. TiO$_2$-mediated photocatalysis may serve as a cost-effective and environmentally green mode of mineralizing organics to yield CO$_2$ and H$_2$O. The photocatalytic activity of a metal oxide semiconductor depends on the ability of the catalyst to create electron–hole pairs, which generate free radicals (e.g. hydroxyl radicals, •OH) that are able to undergo secondary reactions. Fujishima and Honda’s discovery led the surge of interest in TiO$_2$ materials as photocatalysts that we see today.

1.4. Mechanisms of semiconductor-mediated photocatalysis

1.4.1. Electronic mechanism of Photoexcitation

The electronic structure of semiconductor materials is characterized by a filled valence band and empty conduction band at absolute zero (0 K). At any temperature above 0 K, the conduction band is thermally populated by electrons from the valence band according to Fermi-Dirac distribution function ($f(E) \approx \exp[(E-E_\text{F})/k_BT]$, where $f(E)$ is the probability that a conduction band is occupied, $E_\text{F}$ is the Fermi energy, $k_B$ the Boltzmann constant, and $T$ is temperature). The Fermi-Dirac function describes the phenomenon of intrinsic conductivity in pure semiconductors in which the charge carrier concentration is due to the thermalization of the electrons from the valence band. The difference in energy between the anatase conduction and valence bands is the band gap, which for anatase is 3.2 eV. At room temperature, the conduction band is populated with electrons due to thermal excitation and there is corresponding depletion of electrons (e-) from the valence band creating hole states (h+). Both electrons and holes serve as charge carriers in semiconductors. Many semiconductors have band gap energies that are in the range of 0.5-3.5 eV at 298 K.$^{23}$ In the case of titanium dioxide, band gap is 3.2 eV for anatase, 3.0 eV for rutile, and 3.4 eV for brookite.$^{24}$ These values also vary according to
the crystallinity, doping levels, and defects states in the material. Thus, anatase TiO₂ photoexcites under UV light (hv > 3.2 eV) and the minimum band gap excitation wavelength for pure anatase TiO₂ is 387 nm. As discussed, the band gap represents the minimum energy difference between the top of the valence band and the bottom of the conduction band. However, the top of the valence band and the bottom of the conduction band are not generally at the same value of the electron momentum for indirect band gap semiconductors.

In Figure 2 (a) the lowest point of the conduction band occurs at the same value of k (momentum wavevector) as the highest point of the valence band. A direct optical transition is drawn vertically with no change in k. The threshold frequency for absorption by the direct transition determines the energy gap (1).

\[ (1) \, E_g = \hbar \omega \]

The indirect transition (b) involves both a photon and a phonon because the band edges of the conduction and valence bands are separated in k space. The threshold energy for the indirect process in (b) is greater than the true band gap. The absorption threshold for the indirect transition between the band edges is at (2), where Ω is the frequency of an emitted phonon of wave-vector K ≡ -kₐ.

\[ (2) \, \hbar = E_g + \hbar \Omega \]

At higher temperatures phonons are already present; if a phonon is absorbed along with a photon, the threshold energy is (3).²⁵

\[ (3) \, \hbar = E_g - \hbar \Omega \]

One consequence of an indirect band gap is that the absorption onset for a material such as anatase tends to be below \( E_g \) in energy.²⁵ This is because the phonon energy assists the absorption in an indirect band gap semiconductor. A gradual increase
in absorption is seen as a function of energy since the probability of simultaneous photon-phonon interaction is low, but increases as the energy increases since emission of a phonon becomes more probable. Finally, the absorption is steep as a photon is able to take a carrier vertically into the conduction band. Whether a semiconductor has a direct or an indirect bandgap affects the radiative recombination (of hole and electron) lifetime. An indirect semiconductor such as anatase tends to have slower radiative recombination rate than a direct band gap material such as GaAs. Electrons and holes in anatase more often recombine non-radiatively because a phonon is required making the emission or absorption of light. In addition, anatase may have many defect sites at the surface, grain boundaries, and at point defects, all of which may act as non-radiative electron-hole recombination centers. Despite this apparent drawback, the photochemistry of anatase can be controlled by changing the morphology of the crystals and exposing different facets to the environment.

Figure 2. Direct (a) and indirect (b) band gap semiconductors. Note: The figure shows only the threshold transitions. Transitions occur generally between almost all points of the two bands for which wave-vector and energy can be conserved. From reference 25.
Figure 3 shows the photoexcitation and recombination process in the band gap diagram of TiO$_2$. Photoexcitation happens when a valence band electron is promoted to the conduction band resulting in a valence band hole (h$^+$) and conduction band electron (e$'$). As will be described in section 1.5 below, oxidation takes place on the (001) facet of anatase where the h$^+$ reacts with H$_2$O or OH$^-$ and forms OH$^-$. Reduction takes place on the (101) facet through the reaction of O$_2$ with e$'$ and formation of O$_2^*$. Both OH$^-$ and O$_2^*$ are powerful oxidizing agents capable of degrading organics and killing microbes.

**Figure 3.** Schematic showing photoexcitation whereby a valence band electron is promoted to the conduction band resulting valence band hole (h$^+$) and conduction band electron (e$'$). The h$^+$ may react with H$_2$O or OH$^-$ to form OH$^-$. And O$_2$ scavenges e$'$ to form O$_2^*$. From reference 26.

**1.4.2. Chemical Mechanisms of Photodegradation**

During photoexcitation (1), a valence band electron is promoted to the conduction band leaving behind a valence band hole (h$^+$). The photoexcited state of TiO$_2$ is characterized by the chemical species Ti$^{3+}$ and O$^-$ corresponding to trapped e$'$ and h$^+$.
states respectively, which when de-excited have valences of Ti$^{4+}$ and O$^{2-}$ respectively.\textsuperscript{27} The presence of Ti$^{3+}$ states in photoexcited titania have been observed in previous EPR experiments using TiO$_2$ nanopowders.\textsuperscript{27,28} This initial process of photoexcitation occurs on the time scale of 1 fs (10$^{-15}$ s).\textsuperscript{29}

(1) $\text{e}^- \rightarrow h^+ + \cdot$

Photogenerated valence band holes are powerful oxidants ($E = 2.7$ eV) and capable of oxidizing H$_2$O.\textsuperscript{26} Holes react with surface adsorbed H$_2$O to form a water radical cation intermediate: H$_2$O$^+$, which quickly releases a H$^+$ and OH', equation 2. The time scale for OH' formation from the reaction of $h^+$ with H$_2$O is $\sim$ 10 ns.\textsuperscript{26}

(2) $h^+ + H_2O \rightarrow H_2^\cdot \rightarrow H^+ + OH'$

Hydroxyl radicals can also be formed through a mechanism involving molecular oxygen. O$_2$ plays a key role in promoting efficient photo-oxidation and may behave as an electron acceptor, capturing trapped electrons from TiO$_2$ surface to form superoxide ($\cdot O_2^-$) (3).\textsuperscript{30} Through a series of proton and electron transfer steps, the peroxyl radical, HOO$, and finally hydrogen peroxide (H$_2$O$_2$) are formed (4). Hydrogen peroxide readily undergoes hemolytic O-O bond cleavage under illumination to produce 2OH' (5).\textsuperscript{26,30} Thus, TiO$_2$ produces reactive oxygen species (ROS) by electron transfer to and from species in solution and the metal oxide surface. TiO$_2$ is not consumed or degraded in any way in the reactions and only facilitates e- transfer processes under light.

(3) $\cdot + O_2 \rightarrow \cdot O_2^-$

(4) $\cdot O_2^- + 2^+ + e^- \rightarrow H_2O_2$

(5) HOOH $\rightarrow 2OH'$
Hydroxyl radicals are very reactive species with diffusion controlled lifetimes of \(~1\) ns in aqueous media.\(^{26,31}\) Photogenerated OH\(^-\) radicals readily react with organic compounds, R, to yield an organic radical, R\(^'-\), and H\(_2\)O as a byproduct (6).

\[(6)\ R-H + OH^- \rightarrow R' + H_2O\]

Organic radicals, R\(^'\), are unstable species that can instigate a cascade of radical reactions with other organics and result in the formation of smaller byproducts. The mechanisms of these reactions greatly depend on the chemical structures of the species involved \(^{32}\) and they will not be discussed in this paper. Ideally, the reactive organic compounds mineralize completely to form stoichiometric amounts of CO\(_2\) and H\(_2\)O (7).

\[(7)\ z\ R' \rightarrow x\ CO_2 + y\ H_2O\]

However, organic compounds with heteroatoms yield additional inorganic species besides CO\(_2\) and H\(_2\)O. The presence of NO\(_3^-\), SO\(_4^{2-}\), and Cl\(^-\) as a result of the essentially complete photomineralization of nitrogen, sulfur, and chlorine-bearing organic compounds has been reported and confirmed using ion-selective electrodes (ISEs) and titration.\(^{33,34}\) Most of the photocatalytic work with TiO\(_2\) has used nanoscale powders without well-defined morphologies. However, recent work has made it clear that certain facets are more selective for oxidation and reduction processes and thus may allow for more effective photocatalysis.

**1.5. Facet control and reactivity**

The identification of highly active surfaces is the key to understanding the photoreactivity of anatase TiO\(_2\) crystal and also to morphological control of photocatalysts with well-defined crystal facets. Synthesis can be tightly controlled to produce anatase crystals with variety of external morphologies. Figure 4 (the far left crystal) shows the most stable
anatase morphology and the variety of morphologies that anatase may adopt (crystals on the right). Anatase is dominated by the low energy (101) facet in a bipyramid structure, which is capped at each end by the (001) surface. The (001) and (101) surfaces account for 6 and 94% of the total surface area of the truncated bipyramidal crystal, respectively.\cite{35,36}

![Figure 4. Various anatase morphologies. The thermodynamic minimum structure is shown on the left. From reference 35.](image)

However, computational and experimental studies have shown that the anatase \{001\} facets are more reactive than the \{101\} facets especially toward photooxidation. The facet with the higher surface energy tends to be more reactive due to undercoordinated cations. Unfortunately, most often anatase TiO$_2$ crystals are usually dominated by less-reactive \{101\} facets due to their lower surface energy than that of \{001\} facets. It was found by Yang et al\cite{37}, in 2008 that fluorine acts as a surface capping agent by binding to Ti$_{5c}$ and lowers the surface energy of the (001) facet. Lowering the surface energy causes crystal growth to occur much slower in the <001> direction and
faster in the other directions, such as \langle 101 \rangle. Therefore, incorporating fluorine into the synthesis yields crystals with ratios of $\{001\}/\{101\}$ facets that are proportional to the amount of $\text{F}/\text{Ti}$.\textsuperscript{31,38-42} See Figure 5.

Table 1 shows the chemical composition and experimental conditions of extremely of anatase titania micro/nanosheets with exposed $\{001\}$ facets.\textsuperscript{40} As it can be observed when TiF$_4$ was used as a precursor and HF was the capping agent, the $\langle 001 \rangle$ facets percentage highly increased.
Recent work has focused on controlling the morphology of anatase crystals and then evaluating the reactivity of different facets using photochemical methods. Computational and experimental studies have shown that the anatase \{001\} facets are more reactive than the \{101\} facets especially toward photooxidation, while the \{101\} facets have greater reducing power.43 Most often anatase TiO\textsubscript{2} crystals are dominated by less-reactive \{101\} facets due to their lower surface energy than that of \{001\} facets. With the goal of producing crystals with a large fraction of \{001\} facets, Yang et al. predicted using DFT that fluoride would bind to the \{001\} surface and lower the surface energy below that of the \{101\}. Figure 6 shows the calculated ideal \{001\} and \{101\} surfaces of anatase. The \{001\} surface is composed of Ti ions that are 5-coordinate (Ti\textsubscript{5c}) with bridging oxygen atoms that are each coordinated to 3-titanium atoms. By contrast, the \{101\} surface has equal amounts of five- and six-coordinate (Ti\textsubscript{6c}) titanium ions. Fluorine binds to the Ti\textsubscript{5c} ions and stabilizes the \{001\} surface. Without fluorine, the surface energies of the \{001\}, and \{101\} facets are 1.38 Jm\textsuperscript{-2} and 0.84 Jm\textsuperscript{-2}. When fluorine caps the facets, the \{001\} drops below the \{101\} surface at -0.50 Jm\textsuperscript{-2} and -0.20 Jm\textsuperscript{-2}, respectively. Lowering the surface energy causes crystal growth to occur much slower in the \langle001\rangle direction and faster in the other directions, such as \langle101\rangle.38-40 Depending on the synthesis conditions, the \{001\} facet can become the dominant facet exceeding 80% of the total surface area of the crystals.

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<tr>
<td>TiF\textsubscript{4}/TiN/TiB\textsubscript{2}/TiS\textsubscript{2}/TiC/Ti-powder</td>
<td>HF/NH\textsubscript{4}H\textsubscript{2}/NH\textsubscript{4}F</td>
<td>H\textsubscript{2}O</td>
<td>1–5 µm × 1 µm (microsize)</td>
<td>40–60%</td>
</tr>
<tr>
<td>Ti(SO\textsubscript{4})\textsubscript{2}/TBOT</td>
<td>HF</td>
<td>H\textsubscript{2}O</td>
<td>50 nm × 10 nm (nanosize)</td>
<td>18–89%</td>
</tr>
<tr>
<td>TiF\textsubscript{4}/TiCl\textsubscript{4}</td>
<td>HF</td>
<td>H\textsubscript{2}O-alcohol</td>
<td>1.09 mm × 260 nm</td>
<td>50–65%</td>
</tr>
<tr>
<td>TiF\textsubscript{4}/TiCl\textsubscript{4}</td>
<td>HF</td>
<td>H\textsubscript{2}O-IL</td>
<td>microsize</td>
<td>27–82%</td>
</tr>
</tbody>
</table>

Table 1. Chemical composition and experimental conditions of exemplary anatase titania micro-/nanosheets with exposed \{001\} facets. From reference 40.
One key effect caused by the high surface energy is the adsorption of water and other molecules at the surface. Studies have shown that water and methanol adsorb more strongly to the \{001\} than the \{101\} facets once fluorine has been removed from the external surface of the crystals. The fluorine can be removed by washing the anatase with dilute base (e.g., 0.1 M NaOH) or annealing at high temperature. In addition to the enhanced molecular adsorption of \{001\} facets, studies using photoluminescence imaging show that holes diffuse to the \{001\} surfaces and electrons tend to diffuse to the \{101\}.\textsuperscript{44,45} Therefore, oxidation and reduction chemistry take place preferentially on the \{001\} and \{101\} surfaces, respectively.\textsuperscript{35} Since the pioneering work by Yang et al \textsuperscript{46}, much effort has been dedicated to the synthesis and study of anatase TiO\textsubscript{2} crystals with different morphologies and the exploration of these powders for the photocatalytic decomposition of pollutants, hydrogen production, and so on.\textsuperscript{47} In this thesis, the sole structure directing agent is fluorine and both TiF\textsubscript{4} and HF are used as fluorine sources to control both facet shape and thin film growth.

Figure 6. Structure of an ideal (a) (001) surface and (b) ideal (101) surface of TiO\textsubscript{2} calculated using DFT in reference 39.
1.6. Studies on (001) faceted N-doped and N,F co-doped anatase crystals

Recently it was found that TiO$_2$ is an active photocatalyst under visible or UV light when it is doped with nitrogen or a metal oxide like tungsten trioxide. Several groups have reported that TiO$_2$ can be doped with sulfur, which reduces the band gap permitting visible light absorption. In general, there are numerous routes to prepare visible light absorbing TiO$_2$ but one of the most popular and effective dopants is nitrogen.$^{49,50}$

Several groups have explored the visible light response of nitrogen doped anatase TiO$_2$ sheets with dominant {001} facets derived from titanium nitride (TiN).$^{51-53}$ This uses TiN as a titanium source and a source of nitrogen. Crystal growth occurs under solvothermal conditions – HNO$_3$-HF ethanol solution – and results in a nitrogen doped anatase phase with a large percentage of {001} facets, which were induced by surface Ti-F bonds.$^{54}$ The photoactivity of the nitrogen doped anatase TiO$_2$ sheets was estimated by detecting the generated amount of 'OH radicals using terephthalic acid as a hydroxyl radical trap and fluorescent probe.

Asahi et al. reported that N-doped TiO$_2$ shows a significant shift of the absorption edge to a lower energy in the visible light region.$^2$ They calculated densities of states of the substitutional doping of C, N, F, or S for O in the anatase TiO$_2$ crystal, by the full-potential linearized augmented plane wave (FLAPW) formalism in the framework of the local density approximation.$^2$ The substitutional doping of N atom was the most effective because its p states contribute to the band-gap narrowing by mixing with O 2p. Irie et al. suggested that the isolated N 2p narrow band formed above the O 2p valence band was responsible for the visible light but the oxygen vacancy state was not visible light sensitive, Figure 7.$^{55}$
More recently, the simultaneous doping of two kinds of atoms into TiO$_2$ has attracted considerable interest, since it can result in a higher photocatalytic activity and peculiar characteristics compared with single element doping into TiO$_2$. Li et al.$^{56}$ found that N-F co-doped TiO$_2$ nanomaterials had a higher visible-light photocatalytic activity than TiO$_2$ doped solely with nitrogen or fluorine. This can be ascribed to a synergistic effect of two elements co-doping, in which the doped N atoms improved the visible light absorption and the doped F atoms led to enhancement of surface acidity and the absorption of the reactant.

1.7. Substitutional and/or Interstitial N-doping of anatase TiO$_2$

When an oxygen atom in TiO$_2$ is replaced by lighter elements such as nitrogen, carbon, or boron, the semiconductor's valence-band may be depopulated by, one, two or three electrons, respectively. At the same time, the introduction of intra band gap states,
which can produce absorption in the visible region, may occur according to the scheme reported in Figure 8. As the atomic number of the dopant element decreases across the row, the energy of the corresponding 2p states increases due to the smaller nuclear effective charge. According to the calculated position of the impurity states, the N 2p states lies only 0.13 eV above the top of the valence band maximum (VBM) whereas the B 2p states are 2.2 eV above the VBM.57 These impurity states are not filled and contain unpaired electrons, making the species good acceptors. By contrast, in the case of the heavier fluorine dopant the F 2p states lie 1.19 eV below the bottom of the O 2p VB. The extra electron of F with respect to the substituted oxygen atom should be transferred to the empty titanium states. As a matter of fact, such electron is found to be trapped at one Ti site in a 3d state, which is about 0.8 eV below the bottom of the conduction band58,58 in the typical position of impurity states appearing in the band gap of TiO$_2$ upon chemical reduction and formation of Ti$^{3+}$ states.59

The fact that F-doping does not cause any shift in the fundamental absorption edge of TiO$_2$ is consistent with the calculations on F-doped TiO$_2$ performed by Dozzi et al.42 who first claimed that when TiO$_2$ is doped with fluorine, the localized levels composed of F 2p states appear below the valence band and thus cannot contribute to the optical absorption of TiO$_2$. When TiO$_2$ synthesis is performed in the presence of F$^-$ ions, fluorine is naturally incorporated into the bulk and adsorbed to the surface. Fluorine not only affects the crystal habit of anatase, but also increases the size of the crystals and improves the degree of crystallinity, two factors that affect photoactivity.42 Since the crystallinity is improved, a smaller number of bulk defects act as trapping sites and recombination centers of photogenerated charge carriers. Consequently, the charge carriers may diffuse further in the bulk to reach the surface where photocatalytic reactions occur.60
Due to the small atomic size of the non-metal dopant elements B, C, and N, they may diffuse into the semiconductor structure and occupy interstitial positions or bind to lattice atoms. Nitrogen is more electronegative than C or B, and so interstitial nitrogen, $N_i$, preferentially binds to no more than one lattice oxygen whereas boron may bind up to three oxygen atoms.\textsuperscript{57} It turns out that a $N_i$ atom pushes oxygen atoms from the Ti-O-Ti plane toward the interstitial cavity, so that a true NO fragment (holding two extra electrons) is formed. Interstitial nitrogen binds to lattice Ti through its $\pi$ bonding system. In particular, $\pi$ NO states lie below the bottom of the VB, while the $\pi^*$ NO states lie inside the band gap, 0.64 eV above the VBM as shown in figure 8. Thus, interstitial doping with non-metal elements can produce the formation of extra states in the band
gap, which accounts for visible light absorption. It is worth noting that, from the structural point of view, interstitial doping is expected to be more perturbing than substitutional doping, because new X-O bonds (with X representing the dopant element) can be formed, with a consequent higher distortion degree of the original cell. There is a consensus in the literature that the presence in N-doped TiO$_2$ creates localized states within the band gap, which are mainly responsible for the visible light absorption of anion- and in particular for nitrogen-doped TiO$_2$. This fact has been supported and rationalized by combined DFT calculations and EPR studies\textsuperscript{61} evidencing the existence of two possible kinds of nitrogen species, i.e. substitutional and interstitial nitrogen atoms, both thermodynamically favored, depending on the oxidation potential in the doping process. Interstitial doping by fluorine has not been considered, since F is not expected to be oxidized by the lattice and therefore should not bind to oxygen.\textsuperscript{62}

1.8. Research Goal: Utilize visible light for photocatalysis

From the viewpoint of utilizing solar radiation to drive chemical reactions, visible light sensitive TiO$_2$ photocatalysts are highly desired. Although nonmetal doping, in particular nitrogen doping, has shown great potential in shifting visible light absorption of titania, it is challenging to incorporate dopants into anatase TiO$_2$ films rather than powders. Very little work has focused on N-doped TiO$_2$ thin films and in particular films with dominant \{001\} facets that are ideal for photooxidation chemistry. This is because well-faceted anatase TiO$_2$ films usually have very high crystallinity, making it hard or nearly impossible to incorporate significant quantities of dopant atoms into them by mild post-treatment, while the addition of dopant precursors in the reaction medium may inevitably influence the nucleation and growth of anatase TiO$_2$ films so that no desirable TiO$_2$ films could be synthesized. Ichimura et al.\textsuperscript{63} prepared <001> oriented anatase films using fluoride and proved that fluorine increases the (001) surface area, which is great for photooxidation chemistry and this thesis is based on that route to produce doped anatase...
with {001} facets. Because of the wide band gap energy of titanium dioxide, only a small UV fraction of solar light (3-5%) can be utilized for degradation of organic pollutants in water. Therefore, it is of great interest to find ways to extend the absorption wavelength range of titanium dioxide to the visible region without decreasing the photocatalytic activity.

In this study, in order to utilize visible light in photocatalytic reactions, N,F co-doped titanium dioxide films were prepared hydrothermally using two different methods. The methods are distinguished by their nitrogen sources but also their source of titanium. In the titanium nitride method, TiN serves as both a titanium and nitrogen source, but additional Ti is added with TiF$_4$. The second method uses an inexpensive nitrogen containing reagent, sodium azide NaN$_3$, as the nitrogen source and TiF$_4$ as the titanium source. Both the TiN and NaN$_3$ methods use additional HF to direct the growth of anatase films and improve the crystalinity. The substrates used in this work are either evaporated gold or single crystal c-plane sapphire. The resulting anatase films are polycrystalline, continuous, and evenly coat the substrate to a thickness of approximately 700 nm. In addition, the films are unique in that they exhibit strong <001> texture with {001} facets at the surface, and include N-doping to improve visible light absorption. Our study shows that N-doped titanium dioxide films narrow the band gap of anatase and show a shift of the absorption edge to a lower energy in the visible region. This work used GIXRD, SEM, UV-Vis, and XPS to characterize the films produced as a function of reagent concentration and time.
2. Experimental

2.1. Materials Preparation

In order to dope the TiO$_2$ films with nitrogen, two different methods were used. The two methods are distinguished by the different precursors for extrinsic doping with nitrogen, which are titanium nitride (TiN) and sodium azide (NaN$_3$). Titanium nitride (TiN) was used previously by Liu et al.\textsuperscript{64} using a fluoride route to yield N-doped anatase powders with majority \{001\} facets. The use of TiN was the first successful N-doped anatase film synthesis that maintained \{001\} facets at the surface. In this thesis, a novel reagent sodium azide (NaN$_3$) for N-doping anatase is introduced. Sodium azide has several advantages over TiN. For example, NaN$_3$ is inexpensive and soluble in water (pK$_a$ = 4.8). Whereas, TiN does not dissolve completely under the low temperature synthesis conditions (135 °C) employed in this study. The NaN$_3$ compound disintegrates into harmless N$_2$ and Na$^+$ during the course of the reaction. Nitrogen doped TiO$_2$ films prepared with both TiN and NaN$_3$ precursors were synthesized as one-pot hydrothermal and two-step secondary growth routes with the use of hydrofluoric acid (HF) as an extra structure-controlling agent. All other common precursors to N-doped anatase such as urea, ammonium chloride, and guanidine carbonate were not successful using the fluoride route, and were not pursued further.\textsuperscript{65,66}

2.1.1. Preparation of substrates

The single crystal sapphire substrate was cut from a 2” diameter wafer and the plane of the wafer was parallel to the C-plane of sapphire in the hexagonal system. The C-plane sapphire wafer had a flat that was parallel to the A-plane (01-12), Figure 9. The wafer was cut along the A-plane and perpendicular to the cleavage M-plane using a diamond saw. In this way, the substrate could be easily cleaved with a tungsten carbide scoring tool along the M-plane of sapphire. Typical substrate sizes were 20 mm ×20 mm.
The gold on silicon substrates (Au/Si) were prepared by first, cleaning prime grade single-side polished p-type silicon wafers for 15 min in RCA-1 solution, rinsing with ample DI H$_2$O followed by anhydrous ethanol, and then drying under a stream of Ar. (CAUTION! RCA-1 is caustic and requires the user to wear appropriate personal protective equipment!) The wafers were placed into a Veeco bell jar, which was then evacuated and subjected to a 4 h bakeout period. After the pressure dropped to $10^{-7}$ torr, a 5-10 nm layer of Cr was evaporated as an initial wetting layer followed by 150-200 nm layer of Au at a rate 10 A s$^{-1}$.

Figure 9. (a) Commonly used sapphire planes represented in the non-primitive hexagonal crystal system. (b) Sapphire trigonal primitive lattice shown in relation to the hexagonal unit cell. From reference 63.
2.1.2. Preparation of anatase TiO₂ thin films with dominant (001) facets

The direct synthesis of anatase films with (001) reactive facets and [001] preferred orientation was previously studied described by Ichimura et al.67 The anatase films were grown hydrothermally on a gold-coated silicon substrate that was placed vertically in a Teflon liner and immersed in a homogenous solution consisting of 50 mM TiF₄ and 25 mM NaF. The sealed Parr reactor was placed in a furnace and heated for 4 hours at 120 °C and then cooled down to room temperature. In this study the preparation of anatase TiO₂ was similar to this paper, but instead of NaF, 100 mM HF was used when the nitrogen source was TiN. In addition, the concentration of TiF₄ was lowered to 25 mM and the synthesis temperature was 135 °C. Sapphire was used as the substrate for most syntheses.

2.1.3. Preparation of N-doped (001) faceted anatase films

2.1.3.1. One-pot hydrothermal route using TiN, TiF₄, and HF

N,F co-doped TiO₂ thin films were prepared by mounting the substrate - sapphire or gold on silicon - vertically in a Teflon liner and then immersing the substrate into a solution consisting of 40 mM TiN (undissolved), 25 mM TiF₄, and 100 mM HF. The liner was then sealed into a Parr acid digestion reactor and heated at 135 °C for 15 hours. The reactor was removed from the oven and cooled to room temperature. The substrates were removed from the Teflon liner, rinsed thoroughly with deionized water, and dried in air. This as-synthesize film will be referred to as ‘primary growth’. After the film preparation and characterization, the film was annealed to 400 °C in a tube furnace for 2 hours to remove H₂O and improve the film crystallinity.
2.1.3.2. Secondary growth of anatase films using TiN and TiF₄, with HF

Secondary growth refers to a two-step process in which a polycrystalline <001> textured TiO₂ film is first deposited on the substrate. Then in a second step, the N-doped TiO₂ layer is grown epitaxially on top of the first layer. For the first layer, a pure anatase TiO₂ thin film was prepared by mounting the substrate vertically in a Teflon liner and then immersing it into a solution consisting of 25 mM TiF₄ and 100 mM HF and heated to 135 °C for 6 hours (2 hour ramp to temperature, 2 hour hold, and 2 hour cool). Then the second layer, the N-doped TiO₂ film, was grown by mounting the primary growth anatase thin film vertically into a Teflon liner and then immersing it in a solution consisting of 40 mM TiN, 25 mM TiF₄ and 100 mM HF. The liner was then sealed into a Parr reactor and heated at 135 °C for 15 hours. Secondary growth using NaN₃ followed a similar route.

2.1.3.3. One-pot hydrothermal route to N-doped TiO₂ using NaN₃, TiF₄, and HF

The synthesis method for preparing the N-doped films with the NaN₃ precursor is similar to the TiN precursor. The starting solution in this case consisted of 50 mM NaN₃, 25 mM TiF₄, and 50 mM HF. The order of dissolution of compounds is important. Because the pKa of NaN₃ is 4.8 and a typical pH for aqueous solutions consisting of 25 mM TiF₄ is 1.8, NaN₃ does not dissolve in TiF₄ solution. Therefore, NaN₃ is first dissolved in deionized water and then TiF₄ and HF are added. The concentration of HF was lowered in this case since NaN₃ easily dissolves in H₂O compared to TiN, so the need for a concentrated acid to dissolve the starting material was no longer needed. On the other hand, HF was added to the solution to assist the growth of well-formed {001} facets. The synthesis time and temperature was 8 hours at 135 °C.
2.1.3.4. Secondary growth of anatase films using NaN$_3$ and TiF$_4$, with HF

This method is similar to the secondary growth of anatase thin films using TiN as the precursor. After the first undoped TiO$_2$ layer was prepared, the second layer was grown by using a solution consisted of 50 mM NaN$_3$, 25 mM TiF$_4$, and 50 mM HF, held for 8 hours at 135 C, then cooled down to room temperature, and then dried in air. The same procedure described in the one-pot hydrothermal route to N-doped anatase thin films using NaN$_3$ as a precursor was used to prepare secondary growth.

2.2. Materials Characterization

2.2.1. Scanning Electron Microscopy (SEM)

SEM was performed with Carl Zeiss Ultra55 field emission instrument. SEM images were acquired with an Everhart-Thornley (SE2) or annular in-lens secondary electron detector (InLens) at working distances of 4-6 mm and accelerating voltages of 1-5 keV. Each film sample was placed on the center of a 25 mm aluminum stub and secured with brass clips. The positioning of the stubs was carefully aligned so that both top-down and edge-on imaging was possible. The stubs were mounted onto the eight-specimen carousel for top-down imaging and a 45° inclined specimen carousel for edge-on imaging, and then transferred into the SEM. After image acquisition, all SEM plain images were annotated with scale bars. The grain sizes and film thicknesses were determined using SmartTiff software.

2.2.2. X-Ray Diffraction (XRD)

GIXRD patterns were acquired with a Bruker D8 Advance diffractometer using Cu (K$_\alpha$) 1.5406 Å radiation. The diffractometer is equipped with a Goebel mirror and thin
film receiving slit accessories to enable measurements at a grazing angle of 0.5-1°. Diffraction patterns were acquired between 20-80° 2θ with a data spacing of 0.02 at 3 seconds per step. Each film sample was placed onto a Cu holder and placed into the sample cradle of the XRD. The film was aligned with the X-ray beam such that 50% of the intensity passed over the specimen at 0.00 degrees θ and 2θ. The diffraction patterns were fit with the Multipeak-fitting algorithm within the Igor Pro software. The peak positions and relative intensities were recorded.

2.2.3. X-Ray Photoelectron Spectroscopy (XPS)

XPS spectra were acquired with a PHI VersaProbe Scanning XPS Microprobe using Al (Kα) radiation (1486 eV). The PHI is equipped with an argon ion sputter gun to clean the sample surface or to do depth profile analysis. The sapphire substrate tended to charge during x-ray irradiation, which caused the peaks to shift by unpredictable amounts. To eliminate charging, and electron flood gun and argon ion gun with zero accelerating voltage were both used to dissipate charge from the specimen surface. The neutralizer was loaded at 10 eV and the argon gun neutralizer was set at 30 V. The detection limits for all elements except H is ~ 0.01 monolayer, or ~ 0.1% bulk. All spectra were acquired under ultra-high vacuum (UHV) ~ 5 x 10⁻¹⁰ torr. The particular peaks of interest were F1s, N1s, Ti2p³, O1s, and C1s. First, a survey scan was acquired with a pass energy of 117.4 eV, energy step size of 0.5 eV, and the time per step was 30 ms. Then, individual elements were acquired with high resolution scans with a pass energy of 23.5 eV, step size of 0.05 eV , and integration time of 50 ms. Prior to XPS measurement, the samples were cleaned with a plasma cleaner (Gentle Asher™ Model A01; ibss Group, Inc.) for 20 min at SFSU. The air plasma removes most or all of the carbon contamination of the surface. During travel to Stanford, a thin layer of adventitious carbon is re-deposited on this TiO₂ film surface. However, the adventitious carbon film is thin and does not obscure the Ti, O, F, and N peaks. The adventitious
carbon peak is needed as an internal calibration standard. The XPS C1s peak is typically observed at ~285 eV and in this work all spectra were referenced to a C1s peak at 284.7 eV. The XPS spectra were plotted and fit to Gaussian line-shapes with a suitable background function to determine peak positions and linewidths. The C1s peak was fit first, and then the correction from 284.7 eV was applied to all other XPS peaks for a given sample and sample position.

2.2.4. Ultraviolet-Visible Spectroscopy (UV-Vis)

Absorbance spectra of N-doped and un-doped TiO2 films on sapphire were acquired using a Perkin Elmer Lambda 900 UV-Vis-NIR spectrometer. Scans were acquired using a 2 nm slit width between 200-800 nm with a data spacing of 1 nm and integration time of 0.52 seconds. The thin films were mounted on a sample holder with fixed aperture (3 mm x 8 mm...(I have to check)...and a blank sapphire wafer was used as a reference. Reflectance spectra from N-doped and un-doped TiO2 powders were acquired using the same parameters as for the absorbance spectra. However, the N-doped TiO2 powders were placed into 3 mm o.d. quartz tubes with a 1 mm i.d. and spectra were acquired under ambient conditions.

2.2.5. Photooxidative reactivity

To test the photooxidative effectiveness of the anatase thin films treated by different post-processing conditions, each of the as-synthesized and annealed films were used to photooxidize terephthalic acid (TA). The films were first plasma cleaned for 20 min to remove adventitious carbon and then immersed in a 0.1 mM TA solution at pH 12 in a fused silica cuvette. The films were irradiated with a 365 nm source (~1 mW cm⁻²,
Pen Ray) from a distance of 1 cm. The formation of hydroxyl radicals was measured as a function of irradiation time by acquiring the fluorescence spectra of 2-hydroxy terephthalic acid (TAOH). The emission spectra were acquired on a Lambda 55 LS fluorimeter using an excitation wavelength of 315 nm. The maximum emission wavelength of TAOH was 430 nm.

3. Results and discussion

3.1. Characterization of TiO$_2$ films

As mentioned in the experimental section of this thesis, there are two methods for hydrothermally synthesizing N,F co-doped anatase films. The two methods differ in that one method uses TiN as the nitrogen and extra titanium source, while the other method uses sodium azide as the nitrogen source. Two different synthesis methods were also used. One method designated as primary growth (PG) refers to the direct synthesis of the N,F-TiO$_2$ thin film from homogeneous solution. The second method called secondary growth (SG) was a two-step process. First, a TiO$_2$ film was grown on the substrate with TiF$_4$ and HF without a nitrogen precursor. This results in an undoped TiO$_2$ film. The second step used this undoped TiO$_2$ film and either the TiN or NaN$_3$ sources to synthesis a N,F-doped film on top of the TiO$_2$ layer. The synthesis reagents and conditions are summarized below for convenience:

a) TiN P.G.

40 mM TiN + 25 mM TiF$_4$ + 100 mM HF, 135 °C for 15 hours.

b) TiN S.G.

First layer (anatase): 25 mM TiF$_4$ + 100 mM HF, @135 °C for 6 hours.

Second layer: 40 mM TiN + 25 mM TiF$_4$ + 100 mM HF, @135 °C for 15 hours.
c) NaN₃ P.G.

50 mM NaN₃ + 25 mM TiF₄ + 50 mM HF, @135 °C for 8 hours.

d) NaN₃ S.G.

First layer (anatase): 25 mM TiF₄ + 100 mM HF, @135 °C for 6 hours.

Second layer: 50 mM NaN₃ + 25 mM TiF₄ + 50 mM HF, @135 °C for 8 hours.

The films are mostly transparent and display interference fringe patterns on the substrate due to subtle variations in film thickness, see Figure 10. The films are mechanically robust and can be rinsed or sonicated with H₂O and/or ethanol after preparation without the films flaking off the substrate.

Figure 10. Optical image of a N, F co-doped anatase film on sapphire substrate prepared by the TiN method.

During synthesis conditions, TiO₂ nanoparticles nucleate to the substrate surface forming an initial seed layer of random orientation. According to geometric selection, these crystals then grow via a competitive growth mechanism whereby the survival of an individual crystal is determined by its initial orientation and rate of growth on the substrate.⁶⁸
3.2. X-ray Diffraction (XRD)

X-ray diffraction shows that anatase is the only titania phase present after hydrothermal synthesis and after annealing at 400 °C for both the TiN and NaN₃ routes, and for both PG and SG methods. Figure 11 compares the locked-coupled (0-2θ) XRD patterns of the anatase PG and SG films on C-plane sapphire substrate prepared by the TiN and NaN₃ methods. A simulated powder pattern of anatase is also included in Figure 11. Previous work by Marissa Martinez (M.S. Chemistry 2016) showed that anatase films grown on sapphire substrate from aqueous TiF₄ solutions have strong <001> texture, which is accurately described as a heteroepitaxial phenomenon. In the present work, the synthesis conditions that include TiN and NaN₃ still permit the heteroepitaxial match of anatase TiO₂ to c-plane sapphire. The evidence for this assertion is the observation of an intense (004) peak for all samples at ~38 deg. Another peak at 41.7 deg corresponds to the (0006) peak of sapphire, one of the weakest peaks in the corundum powder pattern. The simultaneous observations of the specular reflections of anatase (004) and sapphire (0006) provide strong evidence that the N,F co-doped films exhibit strong preferred orientation with c-axis of anatase parallel to the c-axis of sapphire (TiO₂ [001] || Al₂O₃ [0001]). The only other anatase peak that was observed in the case of secondary growth was a very weak (101) peak at 25.3 deg. The (101) peak may be due to particles that adhere to the film during growth of the initial seed TiO₂ film. Small differences in the peak position of the (004) reflection were observed in the primary growth films. For the PG films prepared by both methods, the (004) reflection was found at 38.1 deg instead of 37.8 deg, which is typical. The peak positions of the PG films was unchanged by annealing and remained +0.3 deg larger than the secondary growth films.

Overall, there is very little difference in the XRD patterns in terms of linewidth and peak positions for the following conditions: (1) Before or after annealing, and (2)
using TiN or NaN$_3$ as sources of Ti and N, and N alone, respectively. A small +0.3 deg shift of the (004) peak was noted for the PG films compared to the SG ones.

Figure 11. Locked coupled XRD patterns of N,F co-doped TiO$_2$ films synthesized by the TiN method S.G./P.G. (a), and NaN$_3$ method S.G./P.G. (b) on sapphire substrates.
The PG and SG growth methods employing NaN$_3$ and TiN as co-reagents were also used to grow TiO$_2$ films on gold. However, when NaN$_3$ was used as a nitrogen source, no TiO$_2$ film was observed to grow. In fact, PG method did not produce any film on gold for either reagent. When a seed TiO$_2$ film was deposited on the gold substrate, then the SG method employing TiN did produce a film. Figure 12 compares the XRD patterns of the TiO$_2$ films on gold substrate acquired by grazing incidence (GI) and locked-coupled diffraction methods. In the GI geometry, the (101), (004), (105), (204), (116), and (215) peaks are observed. Notice that GIXRD pattern is composed mostly of reflections with a significant l-Miller index. Reflections that have Miller indices of the form (hk0) are absent. Both before and after annealing the (004), and (101) peaks are at 37.8 deg and 25.3 deg, respectively. The (004) reflection is more intense for both as-synthesized and annealed film whereas the anatase (101) peak at 25.3° is the most intense in the powder pattern indicating the <001> preferred orientation of the anatase films synthesized on gold substrate.
Figure 12. Grazing incidence (a) and Locked Coupled (b) XRD patterns of N,F co-doped TiO$_2$ film synthesized by TiN S.G. method on a gold substrate.

Figure 12 (b) shows the locked coupled pattern of a N,F-doped TiO$_2$ film on a gold substrate. The as-synthesized film has a very weak (101) peak at 25.3 deg, but after annealing the peak disappears. The most intense peak is the gold (111) at 38.2 deg, while the anatase (004) is a shoulder at 37.8 deg. After annealing, the (004) is slightly sharper and is partially resolved to the low angle side of the gold peak. Other than the (004) and very weak (101) peaks there are no other peaks due to anatase observed for the films synthesized with TiN.

Rocking curve or $\omega$-scans are a type of Bragg diffraction that is used to determine the distribution of orientations of grains about a given reflection. This is done by first setting the detector angle to the Bragg angle $\theta_B$ of interest as the specular reflection such that the scattering vector is perpendicular to the plane of interest. Second, the incident angle is effectively scanned $\pm \Delta \theta$ about $\theta_B$ while keeping the detector angle constant. The resulting linewidth and shape of the rocking curve are quantitative indications of the texture in a polycrystalline sample. The smaller the value of the rocking curve FWHM, the narrower the spread in orientation. For example, the rocking curve of a
single crystal would have a single Gaussian peak with broadening due to the X-ray source and other instrumental effects. This analysis applies to polycrystalline films with fiber texture but may also be used to glean information from heteroepitaxial films.

Figure 13 shows the rocking curve patterns of the films synthesized by both PG and SG methods and TiN and NaN$_3$ starting materials. The general feature of all of the rocking curves is an overall envelope that is about $\sim 4-7^\circ$ deg at the full width half maximum. A few of the rocking curves have distinct peaks. The peak positions are centered at 0.0 deg and the FWHM of all peaks are collected in Table 2.

Figure 13 (a) shows the rocking curve patterns for films synthesized with TiN. The as-synthesized PG film has a FWHM of 5.6$^\circ$. The annealed PG film has 5 peaks that are separated by $\sim 1.5^\circ$ with narrower linewidths that vary from 0.4 – 2.2$^\circ$. The five-peak pattern was observed in phi-scans of the (101) reflection of anatase (measured at the Stanford Synchrotron Radiation Laboratory, SSRL). The pattern is ascribed to a central Bragg reflection indicating perfect heteroepitaxy with two pairs of twinning peaks, possibly with a small lattice tilt induced by twinning.$^{69}$ The SG films synthesized with TiN both have very similar rocking curves with FWHM of 7.7$^\circ$ and 7.6$^\circ$, respectively. These values are very similar to the FWHM observed for TiO$_2$ films on sapphire synthesized with TiF$_4$(aq) and measured at 8 keV on the Bruker D8 advance.

Figure 13 (b) shows the rocking curves for the films synthesized by the NaN$_3$ method. For the S.G. film, both before and after annealing a broad peak is observed with FWHM of 7.1$^\circ$ and 6.8$^\circ$ respectively. For the P.G. film both before and after annealing three peaks are observed. The annealed P.G. film shows less well-defined peaks compared to the same as-synthesized film. Table 2 shows that when the films are annealed the FWHM gets smaller, resulting in narrower peaks. Annealing improves the crystallinity of the films by healing defects in the bulk of the crystal.
Figure 13. Rocking curve scan XRD patterns of N,F co-doped TiO$_2$ films synthesized by the TiN method S.G./P.G. (a) and NaN$_3$ method S.G./P.G. (b) on sapphire substrates.
Table 2. Full width half maximum (FWHM) results for the films synthesized by both TiN and NaN3 methods from rocking curve scan XRD patterns.

<table>
<thead>
<tr>
<th>Film</th>
<th>FWHM (deg)</th>
<th>Peak position (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S.G. TiN As-Synthesized</td>
<td>7.7</td>
<td>0.0</td>
</tr>
<tr>
<td>S.G. TiN Annealed</td>
<td>7.6</td>
<td>0.0</td>
</tr>
<tr>
<td>P.G. TiN As-Synthesized</td>
<td>5.8</td>
<td>0.0</td>
</tr>
<tr>
<td>P.G. TiN Annealed peak 2</td>
<td>2.2</td>
<td>1.9</td>
</tr>
<tr>
<td>P.G. TiN Annealed peak 1</td>
<td>0.33</td>
<td>0.9</td>
</tr>
<tr>
<td>P.G. TiN Annealed peak 0</td>
<td>0.79</td>
<td>0.1</td>
</tr>
<tr>
<td>P.G. TiN Annealed peak 1'</td>
<td>0.45</td>
<td>-0.8</td>
</tr>
<tr>
<td>P.G. TiN Annealed peak 2'</td>
<td>1.14</td>
<td>-1.6</td>
</tr>
<tr>
<td>S.G. NaN3 As-Synthesized</td>
<td>7.2</td>
<td>0.0</td>
</tr>
<tr>
<td>S.G. NaN3 Annealed</td>
<td>6.9</td>
<td>0.0</td>
</tr>
<tr>
<td>P.G. NaN3 As-Synthesized peak 1</td>
<td>1.6</td>
<td>1.9</td>
</tr>
<tr>
<td>P.G. NaN3 As-Synthesized peak 0</td>
<td>0.88</td>
<td>0.4</td>
</tr>
<tr>
<td>P.G. NaN3 As-Synthesized peak 1'</td>
<td>1.55</td>
<td>-1.1</td>
</tr>
<tr>
<td>P.G. NaN3 Annealed peak 1</td>
<td>0.77</td>
<td>1.4</td>
</tr>
<tr>
<td>P.G. NaN3 Annealed peak 0</td>
<td>4.6</td>
<td>0.1</td>
</tr>
<tr>
<td>P.G. NaN3 Annealed peak 1'</td>
<td>1.2</td>
<td>-1.3</td>
</tr>
</tbody>
</table>

One of the most important conclusions of N,F co-doped anatase films that can be derived from the XRD patterns is that they have strong <001> preferred orientation. The N,F-TiO2 films have a heteroepitaxial match to the sapphire substrate that was also observed for films grown from TiF4 (aq) solutions. On gold substrate, the <001> preferred orientation is also pronounced but could not be studied quantitatively by rocking curve analysis due to the overlap with the gold (111) peak.
3.3. Scanning Electron Microscopy (SEM)

Hydrothermal synthesis results in polycrystalline, single-crystal thick nitrogen-doped anatase films with c-axis orientation. The prepared films are continuous and composed of an intergrown network of TiO$_2$ grains. Varying synthesis parameters such as temperature, hold time, and concentrations of precursor materials result in variations in the morphology, grain sizes, and thickness of these films.$^{64}$

Figure 14 shows SEM images of N-doped anatase films prepared by the TiN method. It can be observed that at 135 °C, surface grains have square facets at the surface of the film with intergrowth between adjacent grains as shown in the top-down SEM image in Figure 14 (a). The grains are less than 200 nm in size for a primary growth film. Figure 14 (c) is a top-down image and shows an image of a polycrystalline N,F co-doped anatase film prepared by the secondary growth method. The anatase grains appear square in shape with rounded corners. Each crystal has an edge length of ≤200 nm. The strong texture in the <001> orientation determined by XRD indicates that these square facets are the {001} facets of the tetragonal unit cell.

It is interesting to note the structural difference between the top and bottom of the film. The edge-on images of the cleaved films; Figure 14 (b), reveal that the crystallites near the substrate are ≤ 100 nm in size and grow into a wedge shape that expands near the film surface. The thickness of the film is approximately 600 nm. The areas near the sapphire surface appear to have little or no orientation while the section near the top appears to have a high degree of crystallinity. However, an XRD study of polished TiO$_2$ films on sapphire shows that the even at thickness of ~120 nm, the film exhibits heteroepitaxial behavior.$^{70}$ Even though the grains are small near the substrate surface, the <001> texture is strong. However, it is clear that as the film thickens during growth, that the grains grow along the <001> direction and flair out leading to the square facet at the surface. Figure 14 also shows an edge-on SEM image of a TiO$_2$ film synthesized by a secondary growth TiN method (lower right). It is observed that there is a thin layer,
thickness of approximately 200nm, grown on the first layer. The thickness of the film increases to 730 nm in total thickness. In addition, the second layer has grown epitaxially from the seed layer and appears as short columnar grains that are vertically aligned with respect to the substrate.

Figure 14. Top-down SEM images of N,F co-doped anatase films prepared by the TiN method, primary growth (a), and secondary growth (c). Edge-on images of the same films, primary growth (b), and secondary growth films (d).
Figures 15 (a) and 15 (b) show top-down and edge-on images of a doped anatase film synthesized by a primary growth method using NaN3, respectively. Compared to the TiN method, this film does not have square shaped facets. The surface of the film is composed of very small rounded grains that form a dense but thin film ~200 nm on the sapphire substrate. In previous work and with the TiN synthesis, the square shaped facets correspond to <001> orientation. Nevertheless, XRD patterns have shown that this film has a high degree of <001> preferred orientation, though it is not possible identify facets on these particular grains. Figures 15 (c) and 15 (d) show top-down and edge-on images of a doped anatase film synthesized by a secondary growth method using NaN3 as a
precursor for nitrogen. It can be observed that this film has hemisphere shaped grains that range in diameter from 150 to 230 nm. In this case, the film cross section does not show a clear demarcation between the seed layer and secondary growth layer.

Figure 16 shows an SEM image of annealed films prepared by TiN S.G. method (left) and NaN$_3$ S.G. method (right). The grain size or shape of the facet does not significantly change as a result of annealing, but square holes usually appear within the facets due to loss of water and fluorine. In addition, the annealing process produces micro fractures that propagate along grain boundaries. Cracks likely arise due to stress caused by a mismatch of the thermal expansion coefficients between the substrate and film. The annealed film prepared by the NaN$_3$ S.G. method the grains are slightly coarsened, but the grain size remains the same ~200 nm.

![Figure 16. Top-down SEM image of an annealed film synthesized by the TiN S.G. method (left) and NaN$_3$ S.G. method (right).](image-url)
3.4. X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy was used to investigate the chemical composition of the N,F co-doped TiO₂ films. Since electron photoemission is largely confined to the outer most 10 nm of a metal oxide such as TiO₂, XPS is a surface sensitive technique. High-resolution XPS spectra were deconvoluted to determine the core binding energies of Ti, O, F, and N in the N,F-doped anatase thin films. The deconvolution was carried out by means of a Levenberg-Marquadt algorithm employing a Voigt line shape and a Shirley background using the plugin FitXPS_v0.9 within the Igor Pro program. The XPS peaks were referenced to the C1s peak at 284.8 eV due to adventitious carbon contamination. Most samples that have been exposed to the atmosphere will have a detectable quantity of adventitious carbon contamination, typically with a layer thickness of 1-2nm. Adventitious carbon contamination is commonly used as a charge reference for XPS spectra. Stankovich et al.⁷⁰ showed that the C1s spectrum for adventitious contamination typically has C-C (284.8 eV), C-O-C (~286 eV) and O-C=O (~288.5 eV) components. The C-C peak exhibited a binding energy of 284.8 eV, Figure 17, and was used as a charge correction reference because it is usually the most intense peak.
Figure 18 shows a typical high-resolution scan of C1s core level of a N-F co-doped TiO2 thin film before and after annealing. The C1s binding energies at 284.8 eV and 286 eV are consistent with the presence of C-C and C-O single bonds, respectively. The C-C peak for both spectra is more intense. After annealing and subsequent plasma clean, there is apparently less adventitious carbon on the surface of the film.

Figure 17. A demonstration of binding energies of common chemical states, C1s spectrum of adventitious carbon contamination.

Figure 18. High resolution-scan of C1s core level of a N-F co-doped TiO2 film synthesized by the TiN P.G. method, before (left) and after (right) annealing.
3.4.1. Ti 2p core level

The XPS spectrum of the Ti2p core level obtained form the TiO2 films exhibited Ti2p3/2 and Ti2p1/2 peaks at 458.5 eV and 463.3 eV, respectively, Figure 19. It can be observed there is not much difference between the as-synthesized film and the annealed one. The Ti2p peak splitting is due to spin-orbit components (Δmetal=6.1 eV). The splitting value varies with chemical state (Δnitride=6.0 eV, Δoxide=5.7 eV). The full width at half-maximum (FWHM) linewidth the Ti2p1/2 component is broader than the Ti2p3/2 peak. Post-ionization, the Ti2p1/2 state is very short lived compared to the Ti2p3/2 state and that is caused by the Coster-Kronig effect.64 The binding energies and FWHM for all elements in this study are collected in Table 3.

![Figure 19. High resolution-scan of Ti2p core level of a N-F co-doped TiO2 film synthesized by the TiN P.G. method, before (left) and after (right) annealing.](image)

3.4.2. O1s core level

Oxygen will always be present on samples exposed to the atmosphere, either due to adventitious contamination, oxidation or water. The O1s peak of metal oxides appears at a different binding energy compared to most other oxygen species. The XPS spectrum of the O1s core level obtained from undoped TiO2 films exhibited peaks at 529.6 eV and 530.3 eV. Figure 20 shows core level O1s spectra of N-doped TiO2 thin films prepared by
both nitrogen doping methods. The as-synthesized films have O1s spectra that can be deconvoluted into three peaks while the annealed films have at most two. The as-synthesized film prepared with TiN P.G. method has three peaks at 529.3 eV, 530.1 eV, and 531.5 eV. The O1s peaks of the as-synthesized N,F co-doped TiO2 film synthesized by the NaN3 P.G. method are observed at 529.8 eV, 530.9 eV, and 531.7 eV. The peak at 529.5 eV is assigned to bulk oxygen that is coordinated to three titanium ions of the anatase crystal lattice. All anatase films have the intense lattice O1s peak in common. The peak at ~531 eV corresponds to surface O-H while the peak at ~532 eV corresponds to adsorbed water.71 After the films are annealed the peak due to adsorbed water at ~532 eV is no longer present though a weak OH peak remains.

Figure 20. High resolution-scan of O1s core level of the N-F co-doped TiO2 films synthesized by the TiN P.G. method before (a) and after (b) annealing, and the NaN3 P.G. method before (c) and after (d) annealing.
3.4.3. N1s and F1s core levels

Much experimental effort has been put into nitrogen doping to increase the visible light absorbing properties of TiO2. XPS is the principle means of demonstrating that a particular doping method has worked. The most common N1s signals that are observed from XPS characterization of N-doped TiO2 are peaks at 397 eV and 400 eV.72 The former peak is now generally attributed to nitrogen that substitutes for lattice oxygen and the second one to interstitial nitrogen doping. In early work, it was thought that the signal at 397 eV was responsible for the observed photoactivity under visible light illumination.57,72 In later studies, the XPS peak at 400 eV was frequently observed from N-doped TiO2, especially in samples prepared by chemical methods. These N-TiO2 particles exhibited photocatalytic activity under visible light even in the absence of the XPS peak at 397 eV.2,73,74 This contradiction in the correlation between the XPS signals and photoactivity comes from the fact that these two peaks are not always present simultaneously in N-doped TiO2 photocatalysts and a variety of nitrogen species may be responsible for the N1s XPS spectra. Gyorgy et al.75 studied the nitrogenization on the surface of titanium, and reported that TiN can exist in very different phases. Therefore, the different positions of N1s characteristic peaks may result from the different processes and different conditions. The peak of TiN is generally at 396.9 eV, and the peaks of chemical absorption, NO, NO2 and etc. are at 400 eV or above.75

Recent studies72 indicate that the N1s peak at 399 eV corresponds to the structure of Ti-O-N or N-Ti-O, instead of the structure of Ti-N, N-O or N-N. The N1s characteristic peak of Ti-O-N or Ti-N-O is above 400 eV. Therefore, it is concluded that the peak at 399 eV is responsible for N-Ti-O structure in TiO2 lattice. Figure 21 shows a high resolution scan of the N1s core level of the N-doped TiO2 thin films. Figure 21 (top-left) shows the XPS spectrum of the N1s core level obtained from the N-F co-doped anatase film prepared by the TiN P.G. method. This specimen exhibited a peak at 399.6 eV, which is due to interstitial nitrogen. For N,F co-doped TiO2 films prepared with
NaN₃, one N1s peak was observed at 399.7. This peak is ascribed to interstitial nitrogen in the N-Ti-O configuration while the higher energy peak may be due to trapped N₂ in the lattice. Signals due to molecular nitrogen were observed in samples that were heated under a nitrogen atmosphere. Sodium azide decomposes to give N₂(g) and this could remain trapped in the lattice. After annealing the N1s peak decreases and the signal-to-noise level is poor. Some nitrogen may be lost from the anatase surface as a result of annealing in air.

Figure 21. High resolution-scan of N1s core level of the N-F co-doped TiO₂ films synthesized by TiN P.G. method, before (a) and after (b) annealing and the NaN₃ P.G. method, before (c) and after (d) annealing.
The core F1s spectra for N,F-doped TiO$_2$ are shown in Figure 22. The as-synthesized films have F1s binding energies at 684 eV while the BE of annealed films shifts to slightly higher energy of 684.5 eV. After annealing, some fluorine is removed from the surface as shown by the lower intensity. This phenomenon was also reported in the literature.$^{63}$ Since TiF$_4$ was used as a precursor for TiO$_2$ synthesis and fluorine is a crystallographic controlling agent, the observation of F1s core level BE was expected. Fluorine tends to induce large chemical shifts in other elements, but within a given class of fluorine compounds such as metal fluorides, the shifts in the F1s peak are small. Metal fluorine peaks have binding energies in the range of 684 - 685.5 eV.$^{39}$ Gordon et al. showed that the centroid of the F1s peak at 684.8 ± 0.2 eV is consistent with fluorine bound to the surface of TiO$_2$ and does not indicate the presence of substitutional TiO$_{2-x}$Fx species.$^{39}$ They also suggested that fluorine plays an important role in the formation of oxygen vacancies under the reported synthetic conditions. It is possible that the strong bond between Ti and F (the only bond to titanium stronger than Ti-O) facilitates oxygen vacancy formation. Wang et al.$^{77}$ found that etching the TiO$_2$ surface with HF can produce larger changes in the surface properties than a simple exchange of surface hydroxyl groups. Fluoride can also substitute for surface lattice oxygen, with a consequent increase of surface defects.

![F1s spectra](image-url)
Figure 22. High resolution-scan of F1s core level of the N-F co-doped TiO2 films synthesized by the TiN P.G. method, before (a) and after (b) annealing and the NaN3 P.G. method, before (c) and after (d) annealing.

Table 3. Binding energies (B.E.) and linewidth (FWHM) of O1s, Ti2p3/2 and Ti2p1/2, F1s, and N1s XPS peaks. All values are reported in eV.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BE &amp; FWHM</th>
<th>O1s</th>
<th>Ti2p</th>
<th>F1s</th>
<th>N1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS (TiN P.G.)</td>
<td>BE (eV): 529.3, 530.1, 531.5</td>
<td>458.3, 464.0</td>
<td>684.0</td>
<td>399.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FWHM (eV): 1.2, 1.6, 1.4</td>
<td>1.0, 2.0</td>
<td>1.87</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>AN (TiN P.G.)</td>
<td>BE (eV): 529.7, 529.8</td>
<td>458.5, 464.2</td>
<td>684.3</td>
<td>399.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FWHM (eV): 1.2, 1</td>
<td>1.1, 1.8</td>
<td>2.1</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>AS (TiN S.G.)</td>
<td>BE (eV): 530.1, 531.3</td>
<td>458.5, 464.3</td>
<td>684.7</td>
<td>400, 401.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FWHM (eV): 1, 2.55</td>
<td>1, 1.4</td>
<td>1.85</td>
<td>1.7, 1.3</td>
<td></td>
</tr>
<tr>
<td>AN (TiN S.G.)</td>
<td>BE (eV): 529.5, 530.7, 532.6</td>
<td>458.4, 464.2</td>
<td>684.8</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FWHM (eV): 1.0, 1.2, 1.4</td>
<td>1.0, 1.7</td>
<td>2.4</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>AS (NaN3 P.G.)</td>
<td>BE (eV): 529.8, 530.9, 531.7</td>
<td>458.6, 464.5</td>
<td>684.5</td>
<td>399.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FWHM (eV): 1.2, 1.1, 1.5</td>
<td>1.0, 1.6</td>
<td>1.7</td>
<td>1.9</td>
<td></td>
</tr>
</tbody>
</table>
The XPS data acquired from anatase TiO$_2$ films synthesized from TiN and NaN$_3$ precursors and PG and SG methods provide strong support for the inclusion of nitrogen into the lattice. The nitrogen proves to be in interstitial positions, which is better for visible light absorption. Thus, a new method for incorporating nitrogen into the anatase lattice has been demonstrated. Sodium azide is a common and inexpensive reagent and this method may find application for producing visible light absorbing N-TiO$_2$ films for photocatalysis.

3.5. UV-Vis Spectra

Anatase TiO$_2$ absorbs in the UV region with a weak tail into the visible region as expected for a wide band gap semiconductor that has an indirect band gap energy of 3.2 eV. The transmittance and absorption spectra of the N,F co-doped TiO$_2$ films are compared to an anatase film in Figures 23a and 23b. The anatase film has a transmittance of ~75% through the visible region with an apparent absorption onset at ~400 nm. The N,F-TiO$_2$ PG(NaN$_3$) film has a transmittance of ~68% between 800 and 580 nm. The transmittance then decreases (absorption increases) with a gradual slope until approximately 400 nm when the band edge is reached and direct transitions from the VB to the CV are possible. The N,F-TiO$_2$ PG(TiN) film has a much lower transmittance (higher absorbance) in the visible region of the spectrum with a value of 40% (0.42). The
absorption onset due to N-doping may weakly occur at wavelengths < 500 nm until direct VB-to-CB transitions strongly occur.

\[ TiO_2 \]

\[ NaN_3 \text{ P.G.} \]

\[ TiN \text{ P.G.} \]

\[ TiF_4 \]

\[ HF \]

Figure 23. Transmittance spectra of (001) faceted anatase TiO$_2$ vs. the N,F co-doped TiO$_2$ films synthesized by the NaN$_3$ P.G. and TiN P.G. methods (a), and reflectance absorption spectra from the powders (b).

As previously described, anatase phase TiO$_2$ absorbs at $\lambda < 387$ nm corresponding to a band gap of 3.2 eV. TiO$_2$ materials doped with a heteroatom such as N have increased absorbance in the visible region as a result of induced mid-gap states. The N-doped anatase film synthesized by the NaN$_3$ method shows a lower band gap energy compared to the film synthesized by the TiN method. This suggests that films synthesized by the NaN$_3$ method, can be the most promising method for visible light absorbing thin films. The anatase TiO$_2$ film is showing lower band gap energy, 3.09 eV compared to pure anatase TiO$_2$ which is $\sim$ 3.2 eV. This can be due to fluorine doping of the anatase films due to presence of TiF$_4$ and HF during the synthesis, which creates defects states and excess charge carriers.
3.6. Photooxidation effectiveness of N,F co-doped TiO$_2$ Films under UV irradiation

Anatase TiO$_2$ is an effective photooxidation catalyst for the degradation of organic compounds to provide clean water. The vast majority of studies have used nanoscale powders to measure photooxidative properties for remediation applications. As mentioned before the photocatalytic activity of anatase depends on surface area and intimate contact with the liquid phase. Powders have large surface areas but are not generally morphologically controlled, and they have the significant disadvantage that they must be separated from the purified water. Studies that have focused on facet control have found that the (001) surface is the most photocatalytic active toward oxidation. In the present study, the thin films have only {001} facets at the surface. Practical application of TiO$_2$ for photocatalysis requires a material that is rigidly fixed to a substrate (films) to enhance throughput and facilitate separation.

Very few studies have explored the possibility of using thin films, such as anatase films grown on a transparent substrate such as sapphire probably because of the low surface area of such films.$^{69}$ A common measure of photooxidation effectiveness of TiO$_2$ is based on the production of hydroxyl radicals, •OH, at the semiconductor metal oxide surface. Terephthalic acid (TA) reacts with hydroxyl radicals through diffusion-controlled kinetics to form 2-hydroxyterephthalic acid (TA-OH). TA-OH is highly fluorescent while TA is not, which makes the TA-OH adduct a suitable probe for the formation of hydroxyl radicals. TA has been used extensively to determine the photooxidative effectiveness of TiO$_2$ under high pH conditions.$^{78}$ The amount of photogenerated •OH as a function of UV irradiation time can be used as a measure of the photooxidation effectiveness of N-doped TiO$_2$ films.

Figure 24 shows the growth of the fluorescent signal from TA-OH as a function of irradiation time. Both as-synthesized and annealed films (PG, TiN) produce hydroxyl radicals under 365 nm photolysis. The intensity of the TA-OH adduct increases linearly with time in each case. However, annealed films generate more than five times as many
OH radicals than as-synthesized ones as evidenced by the much greater intensity of the fluorescent probe. This suggests that annealing improved the crystallinity of the thin film and minimized defect trap states allowing the holes to migrate to the \{001\} surface to react with adsorbed water. The increase in TA-OH production due to annealed films was observed previously and was reported in two separate MS theses.\textsuperscript{69,79}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fluorescence.png}
\caption{Fluorescence of TA-OH as generated by an as-synthesized film (right) and an annealed film (left) prepared by the TiN P.G. method. Scans represent photolysis time from bottom to top: 0 min, 20 min, 40 min, 60 min, 80 min, 100 min, and 120 min, respectively.}
\end{figure}

Unfortunately, time constraints prevented additional studies using a visible light source such a solar simulator to carry out additional photooxidation work. In addition, PG films prepared from NaN\textsubscript{3} will be studied. However, it is promising that even N-doped TiO\textsubscript{2} films have such a pronounced photo-oxidation effect despite their low surface area.
4. Summary and Future Work

This thesis has presented a detailed study on synthesizing N,F co-doped anatase TiO_2 thin films on a C-plane sapphire substrate. Two methods were used to accomplish this study. One was a modification of a literature method using TiN as a precursor for nitrogen. The second one was a new method that may improve on the control over doping levels and be very effective for preparing visible light absorbing thin TiO_2 films.

The UV-vis shows that the new method (using NaN_3) for N-doping TiO_2 films has a broad visible absorption out to ~580 nm in addition to the direct transition at about 400 nm. This film shows a lower band gap energy compared to the film synthesized by the TiN method. This suggests that films synthesized by the NaN_3 method are the most promising method to prepare visible light absorbing thin films due to nitrogen doping. XRD confirms that the doped anatase TiO_2 films exhibit strong <001> texture consistent with domain matching epitaxy growth mechanism. The films have ~100% {001} facets at the surface. In testing photooxidation on the various N,F-TiO_2 (001)||Al_2O_3 (001) film surfaces, the main observation is that the film annealed in air and H_2 have superior photooxidation reactivity compared to the as synthesized film. The annealing temperature was 400 °C for two hours. This annealing condition increased the production of hydroxyl radicals due to a reduction in defect trap states. Overall, the results show that photooxidizing effectiveness increases when the doped TiO_2 films have lost fluorine and water during annealing (confirmed with XPS), which ultimately produces films with higher crystallinity. XPS confirms that the films have nitrogen and fluorine on the surface. Annealing decreases the N and F peaks and the signal-to-noise level is poor. Some nitrogen and fluorine may be lost from the anatase surface as a result of annealing in air.

The anatase films produced have a unique combination of <001> texture, {001} facets, and N,F co-doping. These may be the optimal combination for visible light
activated photocatalysis from TiO$_2$ thin films. Future work will refine NaN$_3$ method to improve control over doping of nitrogen to optimal levels for photocatalysis. This will be accomplished by empirical studies that adjust the pH, concentration, and order of addition of reagents. One way to improve the incorporation of nitrogen may be to use a water soluble nitrogen containing ligand on Ti(IV) as the starting material. For example, a complex that contains both F and N$_3$ as ligands, such as (NH$_4$)$_2$TiF$_4$(N$_3$)$_2$ may decompose in water with the concomitant formation of N-TiO$_2$. The fluorine is also built in to the complex and would direct $<$001$>$ growth and $\{001\}$ facets. Such visible light absorbing N-doped films may have additional applications beyond photooxidation chemistry such as hydrogen evolution and CO$_2$ reduction catalysts. In the near term, it will be essential to measure the photooxidation effectiveness of the N-doped TiO$_2$ films using visible light.

5. References


(64) Liu, H.; Jiang, Y.; Zhan, Z.; Tang, B. [XPS characterization of TiN layer on bearing steel surface treated by plasma immersion ion implantation and deposition technique]. *Guang Pu Xue Yu Guang Pu Fen Xi Guang Pu* **2009**, *29* (9), 2585–2589.


